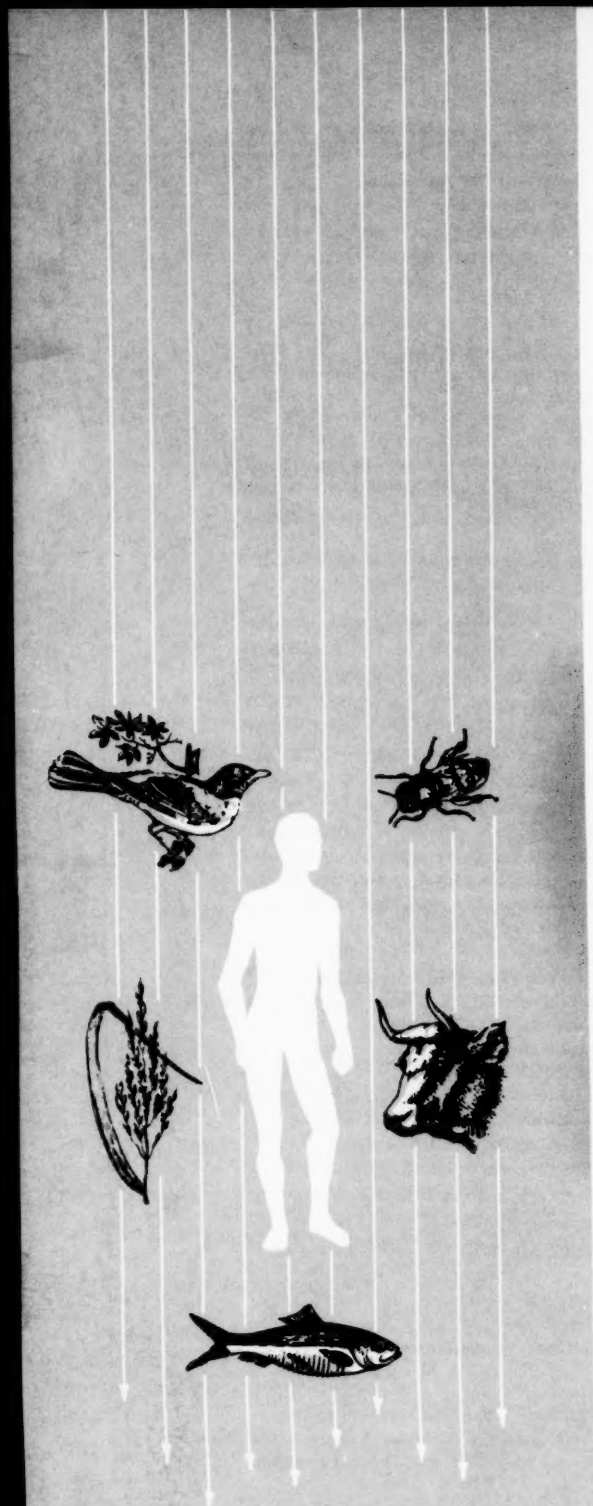

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RESIDUES IN FOOD AND FEED

Organochlorine Insecticide Residues in Vegetables of the Kitakyushu District, Japan—1971-74

M. Suzuki,[1] Y. Yamato,[1] and T. Watanabe [2]

ABSTRACT

The residue levels of organochlorine insecticides BHC, DDT, endrin, and dieldrin in the Kitakyushu District, Japan, were monitored from 1971 to 1974. Agricultural uses of these insecticides were banned in 1970. BHC isomers, α- , β- , γ- , and δ-BHC were detected in all vegetable samples taken; β-BHC residue appeared in the highest levels. The proportions of each BHC isomer in total BHC residues were much different from those in the technical product. Average residue levels of α- , β- , γ- , and δ-BHC, dieldrin, endrin, and DDTR (p,p'-DDT+p,p'-DDE+p,p'-TDE+o,p'-DDT) in 1971 were 0.007, 0.042, 0.010, 0.008, 0.021, 0.010, and 0.041 ppm in radishes, and 0.004, 0.007, 0.009, 0.003, 0.087, 0.031, and 0.009 ppm in cucumbers. Levels found in 1974 were 0.002, 0.003, <0.001, <0.001, 0.005, 0.006, and <0.001 ppm in radishes, and <0.001, 0.001, 0.001, <0.001, 0.008, 0.009, and undetectable in cucumbers. These residues were translocated from the insecticide-contaminated field soils to the vegetables through their roots.

Residue levels of dieldrin and endrin frequently exceeded the pesticide tolerance limits of Japan, but DDTR residues were only slightly above the specified levels.

Introduction

Organochlorine insecticides such as BHC, DDT, aldrin, dieldrin, and endrin have been applied extensively to agricultural fields, orchards, and forests in Japan for the past two decades to control pest damage. BHC was sprayed on rice paddies, and aldrin, dieldrin, endrin, and DDT were applied mainly to vegetable fields to control soil worms or orchard pests.

Japan produced 41,742 tons of BHC in 1967 and 45,695 tons in 1968, and 4,936 tons of DDT in 1968. The nation imported 767 tons of cyclodiene insecticide in 1968. The contamination of cows' milk by BHC, mainly β-BHC, was reported in 1969. Agricultural and forest uses of BHC, DDT, aldrin, dieldrin, and endrin were banned in late 1970 because of the public concern with contaminated foods. During 1971, the first year after the ban, only 2,000 tons of BHC were produced. Thereafter the production of BHC and DDT and the importation of cyclodiene insecticides were almost ceased.

Determination of organochlorine insecticides in foodstuffs using a gas-liquid chromatograph with an electron-capture detector in Japan was initially conducted by Nishimoto et al. (7) in 1966. Many similar studies were conducted subsequently. Because BHC, one of the most heavily used insecticides in Japan, had been applied to the fields without purifying the insecticidally active γ-BHC(lindane), other isomers such as α-, β-, and δ-BHC have been generally found in vegetables. The composition of technical BHC includes 53-70 percent α-BHC, 3-14 percent β-BHC, 11-18 percent γ-BHC, and 6-10 percent δ-BHC. Residues of dieldrin, endrin, and DDTR (*p,p'*–DDT+*p,p'*–DDE+*p,p'*–TDE+*o,p'*–DDT) were also detected in vegetables.

The main objective of the present study was to monitor organochlorine insecticide residues in vegetables commonly cultivated and consumed in the Kitakyushu District, Japan (Fig. 1).

Sampling Procedures

All the vegetable samples were taken directly from the fields in which they were grown according to the schedule in Table 1. Although sampling procedures varied depending on the sample, approximately 1 kg of each vegetable was collected, wrapped in a polyethylene bag, and immediately taken to the laboratory for analysis. Typical samples were a head of cabbage and Chinese cabbage, a root of radish, or three or four roots of turnips and carrots.

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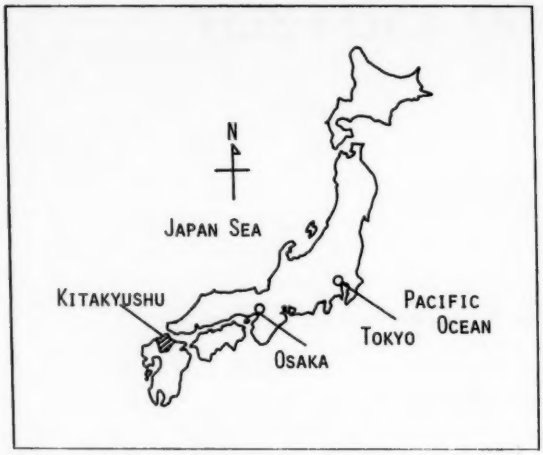

FIGURE 1. *Map of Japan showing the Kitakyushu District*

TABLE 1. *Schedule for sampling vegetables for organochlorine insecticide analyses, Kitakyushu District, Japan—1971-74*

Vegetable	No. Samples Taken	Vegetable	No. Samples Taken
March 21, 1971			
Radish	7	Cabbage	7
Spinach	4		
July 13, 1971			
Cucumber	6	Tomato	5
Eggplant	4	Cabbage	2
September 14, 1971			
Carrot	1	Cabbage	1
Radish	1	Turnip	1
November 5, 1971			
Radish	15	Spinach	6
Chinese Cabbage	8	Turnip	4
Cabbage	7	Carrot	5
July 16, 1972			
Cucumber	8	Radish	1
Eggplant	1	Cabbage	7
November 17, 1972			
Radish	5	Spinach	4
Chinese Cabbage	4	Turnip	4
Cabbage	4		
July 9, 1973			
Cabbage	6	Eggplant	5
Cucumber	5	Carrot	3
December 13, 1973			
Radish	8	Cabbage	5
Chinese Cabbage	6	Turnip	3
September 4, 1974			
Cucumber	4		
November 21, 1974			
Radish	12	Spinach	3
Chinese Cabbage	7	Turnip	5
Cabbage	6		

Analytical Methods

EQUIPMENT AND REAGENTS

Chromatographic columns, 22 x 300 mm

Three-ball Snyder columns with ground glass fittings

5-ml graduated concentrator with ground glass fittings

Shimadzu GC-5AIEE gas chromatograph with dual tritium foil electron-capture detectors

n-Hexane redistilled twice in an all-gas distillation system

Nanograde diethyl ether

Reagent grade anhydrous sodium sulfate heated 2 hours at 625°C to eliminate interferences

Florisil washed thoroughly with distilled water, dried at 110°C, heated at 625°C for 2 hours, deactivated slightly by adding 1 percent distilled water by weight, and mixed well for 30 minutes in a glass-stoppered flask prior to usage

PREPARATION OF SAMPLES

Samples were chopped, mixed thoroughly, and homogenized in a mixer. The root vegetables were washed with cold water to remove adhered soil, and wiped dry. The 100-g homogenized samples were placed in 100-ml beakers, capped with Parafilm, and stored in a refrigerator at –20°C until extraction.

EXTRACTION

All analyses were performed in duplicate and the results represent an average of duplicate analyses. The extraction and partition procedures corresponded to AOAC Official Methods (*1*). However, only 200 ml of 6 percent diethyl ether in n-hexane was used to elute the organochlorine insecticide residues from a florisil column. The eluate was concentrated to approximately 3 ml under a three-ball Snyder column. After addition of heptachlor epoxide as an internal standard, the concentrated eluate was filled up to 5 ml, and 5 μl of the eluate was injected into a gas chromatograph. Recovery was well above 90 percent; results were not corrected.

GAS CHROMATOGRAPHY

Analyses were made with a gas chromatograph equipped with a dual tritium foil electron-capture detector. A multiple column system employing three columns with various polarities was utilized in accordance with the previous report (*12*) to identify and determine residues. The presence of each insecticide was confirmed by comparing the gas-chromatographic retention times of the three columns employed. Operating conditions were:

Column: U-shaped glass, 3 mm ID, 200 cm long

(i) 2 percent OV-17

(ii) 2 percent diethylene glycol succinate—0.5 percent phosphoric acid

(iii) 5 percent Apiezon L grease.

These were coated on 80/100 mesh Gas-Chrom Q.

Carrier gas: prepurified nitrogen at a flow rate of:

(i) 45 ml/min
(ii) 100 ml/min
(iii) 100 ml/min

Temperatures:

Detector: (i) 190°C; (ii) 190°C; (iii) 210°C
Injector: (i) 210°C; (ii) 210°C; (iii) 220°C
Column: (i) 190°C; (ii) 190°C; (iii) 210°C

Retention times of *p,p'*-DDT were approximately 15 minutes on the OV-17 column, 12 minutes on the diethylene glycol succinate–phosphoric acid column, and 12 minutes on the Apiezon L grease column. Twenty-five percent of full-scale deflection was obtained with 0.4×10^{-9} g dieldrin on the Apiezon L grease column. Therefore 0.004 ppm dieldrin in a vegetable sample showed that deflection. Minimum detectable levels of dieldrin, γ-BHC, and *p,p'*-DDT in vegetable samples were 0.0002, 0.0005, and 0.0016 ppm, respectively, through the extraction and gas-chromatographic procedures.

Results and Discussion

The residues detected in vegetable samples are shown in Tables 2-5. BHC isomers were detected in all samples. Insecticide residues in the vegetables might have been transferred from the soil by the roots or taken up from the atmosphere. These insecticides have been prohibited on arable land in Japan since 1970.

BHC isomers were detected in all samples taken because of the high level of contamination of field soils by BHC, one of the most widely used insecticides in the agricultural fields of Japan (*11*). BHC isomers were relatively well absorbed by the vegetables (*13*); β-BHC was dominant among BHC isomers because it was the most persistent in soil (*15*) and the hydrosphere (*10*). The percentage of β-BHC in total BHC was gradually increased; that of α-BHC has decreased. The percentages of BHC isomers in total BHC in 1973 cabbage samples were 7.8 percent α-BHC, 76.5 percent β-BHC, 5.9 percent γ-BHC, and 9.8 percent δ-BHC. The quantities in 1972 radish samples were 2.8 percent α-BHC, 80.0 percent β-BHC, 11:5 percent γ-BHC, and 5.7 per-

TABLE 2. *Organochlorine insecticide residues in vegetables, Kitakyushu District, Japan—1971*

VEGETABLE	NO. SAMPLES	α-BHC	β-BHC	γ-BHC	δ-BHC	DIELDRIN	ENDRIN	DDTR
RADISH	22							
Average, ppm wet weight		0.007	0.042	0.010	0.008	0.021	0.010	0.041
Range, ppm wet weight		T-0.076	0.001-0.401	T-0.049	T-0.031	T-0.136	0.001-0.023	0.002-0.083
Positive samples, %		100.0	100.0	100.0	100.0	68.2	40.9	18.2
CHINESE CABBAGE	8							
Average, ppm wet weight		0.016	0.041	0.025	0.008	0.027	0.003	0.006
Range, ppm wet weight		0.002-0.070	0.002-0.187	0.001-0.142	T-0.031	0.002-0.077	NA	NA
Positive samples, %		100.0	100.0	100.0	100.0	37.5	12.5	12.5
CUCUMBER	6							
Average, ppm wet weight		0.004	0.007	0.009	0.003	0.087	0.031	0.009
Range, ppm wet weight		0.001-0.006	0.003-0.019	0.002-0.018	0.001-0.011	0.002-0.200	0.012-0.067	NA
Positive samples, %		100.0	100.0	100.0	100.0	50.0	50.0	16.7
TOMATO	6							
Average, ppm wet weight		0.003	0.008	0.003	0.001	ND	ND	ND
Range, ppm wet weight		0.002-0.006	0.002-0.030	0.001-0.011	T-0.006	NA	NA	NA
Positive samples, %		100.0	100.0	100.0	100.0	0	0	0
EGGPLANT	6							
Average, ppm wet weight		0.008	0.010	0.006	0.002	0.006	ND	ND
Range, ppm wet weight		0.003-0.026	0.003-0.036	0.002-0.017	0.001-0.006	0.002-0.009	NA	NA
Positive samples, %		100.0	100.0	100.0	100.0	33.3	0	0
CABBAGE	19							
Average, ppm wet weight		0.008	0.014	0.012	0.005	0.005	0.029	0.222
Range, ppm wet weight		0.001-0.037	0.006-0.046	0.002-0.094	T-0.028	0.001-0.009	T-0.076	0.003-0.652
Positive samples, %		100.0	100.0	100.0	100.0	47.4	26.3	15.8
SPINACH	10							
Average, ppm wet weight		0.005	0.040	0.007	0.008	0.008	0.063	0.023
Range, ppm wet weight		0.001-0.055	0.001-0.072	0.001-0.016	0.001-0.021	0.001-0.027	0.006-0.121	0.005-0.036
Positive samples, %		100.0	100.0	100.0	100.0	80.0	20.0	30.0
TURNIP	5							
Average, ppm wet weight		0.001	0.016	0.002	0.001	0.004	0.002	0.020
Range, ppm wet weight		T-0.003	0.002-0.050	T-0.004	T-0.002	0.003-0.005	NA	0.009-0.031
Positive samples, %		100.0	100.0	100.0	100.0	60.0	20.0	40.0
CARROT	6							
Average, ppm wet weight		0.041	0.134	0.021	0.026	0.035	0.017	0.003
Range, ppm wet weight		0.002-0.192	0.012-0.350	0.001-0.083	0.001-0.068	T-0.110	NA	NA
Positive samples, %		100.0	100.0	100.0	100.0	83.3	16.7	16.7

NOTE: T = trace (<0.001 ppm wet weight).
ND = not detected.
NA = not applicable.

TABLE 3. *Organochlorine insecticide residues in vegetables, Kitakyushu District, Japan—1972*

VEGETABLE	NO. SAMPLES	α-BHC	β-BHC	γ-BHC	δ-BHC	DIELDRIN	ENDRIN	DDTR
RADISH	6							
Average, ppm wet weight		0.001	0.028	0.004	0.002	0.018	0.008	ND
Range, ppm wet weight		0.001-0.004	0.004-0.072	0.002-0.007	T-0.007	0.009-0.027	0.004-0.010	NA
Positive samples, %		100.0	100.0	100.0	100.0	33.3	50.0	0
CHINESE CABBAGE	4							
Average, ppm wet weight		0.002	0.010	0.002	0.001	0.003	0.001	ND
Range, ppm wet weight		0.001-0.003	0.004-0.019	T-0.003	T-0.003	0.001-0.005	NA	NA
Positive samples, %		100.0	100.0	100.0	100.0	50.0	25.0	0
CABBAGE	11							
Average, ppm wet weight		0.030	0.068	0.010	0.014	0.006	0.004	0.016
Range, ppm wet weight		0.001-0.200	0.003-0.169	0.002-0.043	T-0.088	0.003-0.010	0.002-0.007	0.002-0.045
Positive samples, %		100.0	100.0	100.0	100.0	27.2	18.2	27.2
SPINACH	4							
Average, ppm wet weight		0.005	0.009	0.004	0.003	0.068	ND	0.013
Range, ppm wet weight		0.003-0.009	0.013-0.072	0.002-0.010	0.001-0.008	0.014-0.122	NA	0.011-0.015
Positive samples, %		100.0	100.0	100.0	100.0	50.0	0	50.0
TURNIP	4							
Average, ppm wet weight		0.001	0.011	0.001	T	0.005	0.016	ND
Range, ppm wet weight		T-0.001	0.007-0.016	NA	T-0.001	0.001-0.008	0.001-0.030	NA
Positive samples, %		100.0	100.0	100.0	100.0	50.0	50.0	0
CUCUMBER	8							
Average, ppm wet weight		0.014	0.016	0.005	0.003	0.043	0.014	ND
Range, ppm wet weight		0.002-0.031	0.004-0.059	0.002-0.008	0.001-0.005	0.004-0.129	NA	NA
Positive samples, %		100.0	100.0	100.0	100.0	87.5	12.5	0

NOTE: T = trace (<0.001 ppm wet weight).
ND = not detected.
NA = not applicable.

TABLE 4. *Organochlorine insecticide residues in vegetables, Kitakyushu District, Japan—1973*

VEGETABLE	NO. SAMPLES	α-BHC	β-BHC	γ-BHC	δ-BHC	DIELDRIN	ENDRIN	DDTR
RADISH	8							
Average, ppm wet weight		0.001	0.003	0.001	T	0.003	0.005	0.003
Range, ppm wet weight		T-0.003	T-0.013	T-0.001	NA	T-0.007	T-0.010	T-0.008
Positive samples, %		100.0	100.0	100.0	100.0	50.0	62.5	37.5
CHINESE CABBAGE	6							
Average, ppm wet weight		0.033	0.009	0.007	0.004	T	0.002	ND
Range, ppm wet weight		T-0.188	T-0.037	T-0.038	T-0.022	T-0.001	0.001-0.003	NA
Positive samples, %		100.0	100.0	100.0	100.0	50.0	50.0	0
CABBAGE	11							
Average, ppm wet weight		0.004	0.039	0.003	0.005	0.002	0.003	0.018
Range, ppm wet weight		0.001-0.020	0.002-0.238	0.001-0.012	T-0.036	T-0.006	T-0.005	T-0.078
Positive samples, %		100.0	100.0	100.0	100.0	45.5	54.5	54.5
TURNIP	3							
Average, ppm wet weight		0.001	0.004	T	T	0.002	ND	ND
Range, ppm wet weight		T-0.003	0.002-0.006	T-0.001	T-0.001	0.001-0.003	NA	NA
Positive samples, %		100.0	100.0	100.0	100.0	66.7	0	0
CUCUMBER	5							
Average, ppm wet weight		0.002	0.003	0.002	0.001	0.043	0.016	0.005
Range. ppm wet weight		0.001-0.004	0.001-0.006	0.001-0.007	0.001-0.002	0.001-0.133	0.005-0.027	0.003-0.007
Positive samples, %		100.0	100.0	100.0	100.0	100.0	80.0	80.0
EGGPLANT	5							
Average, ppm wet weight		0.001	T	0.001	0.001	0.001	ND	ND
Range, ppm wet weight		T-0.002	T-0.001	T-0.002	T-0.005	NA	NA	NA
Positive samples, %		100.0	100.0	100.0	100.0	20.0	0	0
CARROT	3							
Average, ppm wet weight		0.013	0.142	0.010	0.013	ND	ND	ND
Range, ppm wet weight		0.004-0.020	0.034-0.275	T-0.021	T-0.024	NA	NA	NA
Positive samples, %		100.0	100.0	100.0	100.0	0	0	0

NOTE: T = trace (<0.001 ppm wet weight).
ND = not detected.
NA = not applicable.

TABLE 5. *Organochlorine insecticide residues in vegetables, Kitakyushu District, Japan—1974*

VEGETABLE	NO. SAMPLES	α-BHC	β-BHC	γ-BHC	δ-BHC	DIELDRIN	ENDRIN	DDTR
RADISH	12							
Average, ppm wet weight		0.002	0.003	T	T	0.005	0.006	T
Range, ppm wet weight		T-0.004	T-0.015	T-0.001	NA	T-0.021	0.001-0.010	NA
Positive samples, %		100.0	100.0	100.0	100.0	50.0	16.7	16.7
CHINESE CABBAGE	7							
Average, ppm wet weight		0.712	0.095	0.224	0.054	0.001	0.002	ND
Range, ppm wet weight		T-3.560	0.001-0.348	T-1.200	T-0.198	NA	NA	NA
Positive samples, %		100.0	100.0	100.0	100.0	28.6	14.3	0
CABBAGE	6							
Average, ppm wet weight		0.004	0.026	0.002	0.001	0.001	0.001	0.002
Range, ppm wet weight		0.001-0.006	0.001-0.098	0.001-0.002	T-0.002	NA	NA	T-0.007
Positive samples, %		100.0	100.0	100.0	100.0	33.3	16.7	83.3
SPINACH	3							
Average, ppm wet weight		0.002	0.128	0.003	0.008	0.012	ND	0.016
Range, ppm wet weight		0.001-0.004	0.003-0.285	0.001-0.008	T-0.022	0.001-0.030	NA	T-0.032
Positive samples, %		100.0	100.0	100.0	100.0	66.7	0	66.7
TURNIP	5							
Average, ppm wet weight		T	0.001	0.001	T	0.001	0.001	0.002
Range, ppm wet weight		T-0.001	T-0.004	T-0.003	NA	NA	NA	T-0.005
Positive samples, %		100.0	100.0	100.0	100.0	40.0	20.0	60.0
CUCUMBER	4							
Average, ppm wet weight		T	0.001	0.001	T	0.008	0.009	ND
Range, ppm wet weight		T-0.001	T-0.002	T-0.001	NA	T-0.025	0.003-0.014	NA
Positive samples, %		100.0	100.0	100.0	100.0	100.0	50.0	0

NOTE: T = trace (<0.01 ppm wet weight).
ND = not detected.
NA = not applicable.

cent δ-BHC. Percentages of BHC isomers in the commercial insecticide in Japan were 53-70 percent α-BHC, 3-14 percent β-BHC, 11-18 percent γ-BHC, and 6-10 percent δ-BHC.

Authors speculate that the percentage of β-BHC increased because of its lower vapor pressure, which is 2.8×10^{-7} mmHg. The vapor pressure of α-, γ-, and δ-BHC are 2.5×10^{-5}, 9.4×10^{-6}, and 1.7×10^{-5} mmHg, respectively (*16*); β-BHC was also the most persistent residue among BHC isomers in the soil (*9,15*). The average BHC residue was composed of 7.5 percent α-BHC, 63.2 percent β-BHC, 12.1 percent γ-BHC, and 17.2 percent δ-BHC 19 months after BHC application to a sandy field (2 kg 3 percent γ-BHC a.i./1000 m^2) (*15*).

Eggplant, tomatoes, and cucumbers, vegetables which grew above ground, had lower residues of the BHC isomers than had the root vegetables. Among root vegetables, carrots had the highest BHC residue levels because of the vegetables' high translocation capability. With slight exceptions, BHC residue levels in the vegetables have gradually decreased during the 4-year period, particularly in radishes and turnips.

Residues of dieldrin and endrin were frequently detected at comparatively high levels. In particular, high dieldrin residue levels were found in cucumbers and carrots, which are known to absorb high quantities of dieldrin (*4*). In Japan the cucumber fields had been heavily treated with cyclodiene insecticides; therefore, dieldrin and endrin residue levels were high in the soil of cucumber fields. Photodieldrin, a photoconversion product (*8*) and microbially degraded metabolite (*5*) of dieldrin, was identified in the cucumber field soils (*14*), but no residue could be found in the cucumbers. During the 4-year survey, residues of dieldrin and endrin were detected in vegetables in the following percentages: 1971, 54.2 and 25.0; 1972, 48.6 and 24.3; 1973, 48.8 and 43.9; 1974, 48.6 and 18.9. These percentages were consistent for dieldrin but a disproportionately high occurrence of endrin was found in 1973. No aldrin residues were detected in any vegetable samples, which suggests that aldrin was converted to dieldrin by plant enzymes such as mixed function oxidases or vapor phase oxidation in the atmospheric environment.

Residues of DDTR were detected in vegetables in the following percentages: 1971, 17.5; 1972, 13.5; 1973, 31.7; 1974, 32.4. These residue levels scarcely exceeded the pesticide residue tolerance (Table 6); DDTR in field soil was generally not translocated into vegetables (*11*).

TABLE 6. *Pesticide residue tolerances set by Japanese government for certain vegetables*

VEGETABLE	RESIDUES, PPM			
	TOTAL BHC	DDTR	ENDRIN	ALDRIN/DIELDRIN
Radish	0.2	0.2	ND	0.02
Chinese Cabbage	0.2	0.2	ND	0.02
Cabbage	0.2	0.2	ND	0.02
Spinach	0.2	0.2	ND	ND
Turnip	0.2	0.2	*	*
Cucumber	0.2	0.2	ND	0.02
Tomato	0.2	0.2	ND	0.02
Eggplant	0.2	0.2	ND	0.02
Carrot	*	*	*	*

NOTE: DDTR = DDT+DDE+TDE.
ND = not detectable.
* = not legislated.

The quantity of samples with insecticide residue levels exceeding the pesticide residue tolerance set by the Japanese government was 25.0 percent in 1971, 35.1 percent in 1972, 36.6 percent in 1973, and 27.0 percent in 1974. Tolerances for carrots and turnips have not yet been set. The percentages of samples exceeding the tolerance limit did not change markedly during the study. A large portion of the excesses are attributed to the high dieldrin and endrin levels. Residues in the vegetables were transported from contaminated field soil through the roots of the vegetables (*4,13*) or absorbed from the atmosphere, or evaporated or codistilled from field soil surface (*6*). Because dieldrin and endrin are two of the most toxic agricultural chemicals, the recommended maximum acceptable daily intake set by the Food and Agricultural Organization/World Health Organization (FAO/WHO) for dieldrin was 0.0001 mg/kg body weight (*18*). Elimination of these insecticides from the environment is desirable.

Uyeta et al. (*17*) reported that the daily intake of dieldrin in total diet by residents of the Kochi Prefecture in Japan was 4.8 μg/day. Daily intakes of 2.6 μg/day in Italy (*2*) and 6.6 μg/day in Great Britain (*3*) have been established. These values range from 37.1 to 94.3 percent of the FAO/WHO maximum acceptable daily intake of a person weighing 70 kg. The daily dieldrin content in the diet of residents of the Kitakyushu District was approximately the same as that of the Kochi Prefecture residents. DDT is less toxic than dieldrin. It has a higher recommended maximum acceptable daily intake (0.01 mg/kg body weight) and a higher maximum daily intake acceptable for a person weighing 70 kg.

Comparing the residue levels in the vegetable samples with those found by Nishimoto et al. (*7*) which were published when organochlorine insecticides were still used, no distinct differences were observed, especially in the residue levels of dieldrin and endrin. For example, Nishimoto et al. reported that 0.007-0.015 ppm endrin was detected in four of five radish samples and 0.006 ppm γ-BHC was found in one of five cucumber samples (*7*).

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Organochlorine Pesticide Residues in Sugarbeet Pulps and Molasses from 16 States, 1971

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ABSTRACT

Sugarbeet pulp and molasses from 57 processing plants in 16 States were sampled for pesticide residues. No molasses samples contained detectable pesticide residues, but about 15 percent of the pulp samples contained low levels of dieldrin, toxaphene, or DDT and its degradation products. Sugarbeet pulp, when used as animal feed, can be a source of pesticidal contamination of human food.

Introduction

Sugarbeet pulp and molasses are waste products obtained from the processing of sugarbeets and sold directly in large quantity as cattle feed. The molasses is also used as an important medium for fermentation, particularly for the production of citric acid, a common food additive. Muns, Stone, and Foley (*3*) reported that 3 lb/a (3.4 kg/ha.) toxaphene applied as a soil treatment resulted in residues of less than 0.4 ppm toxaphene in mature sugarbeets. Johnson and Bischel (*2*) emphasized the potential public health problem of residues in sugarbeet byproducts and found that DDT residues in mature whole beets were less than 0.2 ppm. In studying the fate of aldrin, dieldrin, and endrin residues during partial laboratory processing of raw sugarbeets, Walker et al. (*6*) found that the dried pulp contained the major portion of these pesticide residues. However, published reports of pesticide residues in sugarbeet pulp and molasses from industrial processing plants are rare.

Because of their uses in animal feed additives, sugarbeet pulp and molasses can be significant pathways for pesticide residue transport. The objective of this study was to determine the pesticide residue levels in pulp, molasses, and other commercial products from industrial sugarbeet processing plants.

Processing Technology

Sugarbeets are usually washed and transported from storage areas to the processing plant by small canals filled with warm water. In the plant, the beets are rewashed, sliced, and dropped into a diffuser which countercurrently extracts the beet sugar with water at 79.4°C. The pulp portion is dried and sold as cattle feed. The resulting raw juice is purified with milk of lime, carbon dioxide, and filtration. Soybean oil, tallow, or other oils are added in this purification step to reduce foaming (*4*). Concentrated Steffens' filtrate comes from the process and is later stripped of its residual sugar contents by crystallization.

Materials and Sampling Methods

Sugarbeet processing plants were identified in 16 States: Arizona, California, Colorado, Idaho, Iowa, Kansas, Michigan, Minnesota, Montana, Nebraska, North Dakota, Ohio, Oregon, Utah, Washington, and Wyoming. All samples in this study were collected from the 57 processing plants in operation at the study's initiation.

Samples were collected in the fall of 1970. The primary products sampled were sugarbeet pulp, molasses, and related processing materials such as soybean oil, tallow, and Steffens' filtrate. The sampling methods of the U.S. Department of Agriculture were employed (*5*). The number and kinds of samples are listed by State in Table 1.

Chemical Analysis

All analyses reported in this paper were conducted at the Pesticide Monitoring Laboratory, Bay St. Louis, Miss. The extraction of samples of sugarbeet pulp, soy-

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TABLE 1. *Number and type of samples collected by State, 1971*

State	No. Plants	No. Samples				
		Pulp	Molasses	Soybean Oil	Tallow	C.S.F.[1]
Arizona	1	2	—	—	—	—
California	10	20	3	—	—	—
Colorado	10	20	14	—	—	—
Idaho	4	8	8	—	—	8
Iowa	1	2	2	2	—	—
Kansas	2	4	—	—	—	—
Michigan	5	10	—	—	—	—
Minnesota	4	8	8	—	—	—
Montana	3	6	3	—	—	3
Nebraska	4	8	7	—	—	4
North Dakota	1	2	2	2	—	—
Ohio	3	6	2	—	1	—
Oregon	1	2	2	—	—	—
Utah	3	6	6	—	—	—
Washington	2	4	4	—	—	—
Wyoming	3	6	4	—	—	—
TOTAL	57	114	65	4	1	15

NOTE: — = no sample collected.
[1] Concentrated Steffens' filtrate.

bean oil, and tallow was similar to methods reported previously (*1*).

The molasses and filtrate were extracted by weighing a 20-g sample into a 100-ml beaker and then thinning with 20 ml distilled water so that less than 5 percent of the sample adhered to the beaker. This mixture was poured into a 500-ml separatory funnel and 150 ml redistilled hexane was added and mixed a few seconds by shaking. Fifty ml isopropanol was added, and the mixture was shaken again and allowed to settle. The mixture was then washed three times with 150 ml distilled water and the aqueous layers were discarded. The hexane layer was then filtered through a sodium sulfate filter tube into a 500-ml conical jointed flask. The excess solvent was evaporated through a Snyder column to about 5 ml and transferred to a graduated centrifuge tube or other container. The extract was diluted to 10 ml with hexane and stored at low temperature for gas chromatography. No cleanup was necessary.

Analyses were performed on gas chromatographs equipped with tritium foil electron affinity detectors for organochlorine compounds and flame phytometric detectors for organophosphorus compounds. Pesticides and related chemicals detectable by these methods are listed in Table 2. A multiple-column system employing polar and nonpolar stationary phases was used to identify the pesticides. Dual-column gas chromatography was employed for each sample: the main column and one of the two alternative supplementary columns. Instrument parameters were:

Columns

glass, 6 mm OD by 4 mm ID, 183 cm long packed with one of the following:

1.5 percent OV-17/1.95 percent QF-1 on 100/120 mesh diatoport (alternative and supplementary column)

3 percent DC-200 on 100/120 mesh gas-chrom Q (main column)

9 percent QF-1 on 100/120 mesh diatoport (alternative and supplementary column)

Carrier Gases

5 percent methane-argon at a flow rate of 80 ml/min

Prepurified nitrogen at a flow rate of 80 ml/min

Temperatures

Detector	200°C
Injection port	250°C
Column QF-1	166°C
Column DC-200	170°-175°C
Mixed column	185°-190°C

TABLE 2. *Chemical compounds detectable by the analytical method used in the present study*

Organochlorine Compounds	Organophosphorus Compounds
Aldrin	DEF
Benzene hexachloride isomers	Diazinon
Dieldrin	Ethion
o,p'-DDE	Ethyl parathion
p,p'-DDE	Malathion
o,p'-TDE	Methyl parathion
p,p'-TDE	Phorate
o,p'-DDT	Trithion
p,p'-DDT	
Endrin	
Heptachlor	
Heptachlor epoxide	
Polychlorinated biphenyls	
Technical chlordane	
Toxaphene	
Trifluralin	

Generally, the limit of minimum detection was 0.01 ppm. Mixed pesticides such as polychlorinated biphenyls, toxaphene, and chlordane are exceptions, and the limits for these pesticides range from 0.03 to 0.05 ppm.

RECOVERY

Recovery rates from sugarbeet pulp ranged from 89 to 105 percent except heptachlor epoxide which was 82 percent. Recovery rates from molasses and filtrate ranged from 83 to 88 percent with an average of 87 percent. Results presented here were corrected for recovery.

Results and Discussion

All residue results were reported on the sample as it had been received. Nearly 15 percent of the 114 pulp samples contained pesticide residues as shown in Table 3. Residues of *p,p'*-DDE, *o,p'*-DDT, *p,p'*-DDT, dieldrin, toxaphene, and *o,p'*-DDE were found but the arithmetic mean concentrations of all these residues were less than 0.01 ppm.

The mean dieldrin residue value for pulp was below 0.01 ppm and maximum value detected was 0.01 ppm. Walker et al. (*6*) reported the dieldrin residue of dried sugarbeet pulp for three different pesticide treatments

TABLE 3. *Arithmetic mean and range of pesticide residues in sugarbeet pulp and related materials from processing plants*

Material	No. Analyses	Positive Samples, %	*o,p'*-DDE Mean	*o,p'*-DDE Range	*p,p'*-DDE Mean	*p,p'*-DDE Range	*o,p'*-DDT Mean	*o,p'*-DDT Range	*p,p'*-DDT Mean	*p,p'*-DDT Range	Dieldrin Mean	Dieldrin Range	Toxaphene Mean	Toxaphene Range	Heptachlor Epoxide Mean	Heptachlor Epoxide Range
Pulp	114	14.7	<0.01	ND-0.01	<0.01	ND-0.16	<0.01	ND-0.01	<0.01	ND-0.05	<0.01	ND-0.01	<0.03	ND-0.34	ND	ND
Molasses	65	0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Soybean Oil	4	50.0	ND	ND	ND	ND	ND	ND	ND	ND	0.02	ND-0.05	ND	ND	<0.01	ND-0.01
Tallow	1	100.0	ND	ND	ND	ND	ND	ND	ND	ND	0.01	NA	ND	ND	ND	ND
C.S.F.[1]	15	0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

NOTE: ND = not detected.
NA = not applicable.
Limit of minimum detection is generally 0.01 ppm except for toxaphene, which ranges from 0.03 to 0.05 ppm.
All residues were reported on the sample as it had been received.

[1] Concentrated Steffens' filtrate.

of soil in their pilot laboratory study; the mean of their three dieldrin residue values was 1.096 ppm and the range was 0.089-1.712 ppm. The difference between findings of these two studies may reflect differences in handling and processing practices between industrial processing plants and the pilot laboratory.

No pesticide residues were found in samples of molasses or concentrated Steffens' filtrate, a fact which may result from the manufacturing process. Pulp is extracted with water at 79.4°C. Since chlorinated hydrocarbons are quite insoluble in water, much of the pesticide residue may remain in the pulp. Even if residues were found in the juice, it is highly probable that the severe treatments with milk of lime, sulfur dioxide, and activated carbon would remove or destroy residues. Because the concentrated Steffens' filtrate and molasses are both derivatives of juice, it is not surprising that no pesticide residues could be detected.

The detection of dieldrin and heptachlor epoxide in soybean oil is consistent with the result of a previous study (*1*) which showed that soybeans contained mean levels of 0.12 ppm dieldrin and less than 0.01 ppm heptachlor epoxide.

All pesticide residues detected in the study of sugarbeet pulp, that is, DDT, dieldrin, and toxaphene, had been commonly applied to soil or mixed with dry seed prior to planting for control of various sugarbeet pests such as wireworms, root maggots, and cutworms. Therefore, the detected residues are indication of cause and effect of pesticide application.

Conclusion

Use of sugarbeet pulp as cattle feed presents a potential problem of pesticide entry into cattle and eventually into the human food chain. However, the small amount of residues present in the pulp may never build up enough in the human food chain to endanger health. Molasses from sugarbeet processing does not present such a problem.

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RESIDUES IN FISH, WILDLIFE, AND ESTUARIES

Organochlorine Residues in Three Bat Species from Four Localities in Maryland and West Virginia, 1973 [1]

Donald R. Clark, Jr., and Richard M. Prouty

ABSTRACT

In 1973, 119 bats of three species were collected from four localities in Maryland and West Virginia. The collection included 43 big brown bats (Eptesicus fuscus), *43 little brown brown bats* (Myotis lucifugus), *and 33 eastern pipistrelles* (Pipistrellus subflavus). *The bats were collected from Round Top Mountain, Washington Co., Md.; Trout Cave, Pendleton Co., W. Va.; Montpelier Barn, Prince Georges Co., Md.; and North East Methodist Church in Cecil Co., Md. Residues of ΣDDT were highest in carcasses of bats from Round Top Mountain, which is surrounded by apple orchards. Bats from Trout Cave had the lowest residues, a circumstance which probably reflects the absence of agriculture and industry in the area. A polychlorinated biphenyl (PCB) and oxychlordane were highest at Montpelier Barn. Sources of the PCB are unknown, but chlordane is used against termites and in gardening at nearby housing developments. Residues in bats from North East Methodist Church were low except for dieldrin. Among species, little brown bats usually had the highest residue concentrations in their carcasses, whereas big brown bats had the lowest.*

When DDE in carcass fat of all species was above 60-90 ppm, it became measurable in brain tissue. Above 60-90 ppm, DDE levels in brains rose with increasing levels in carcass lipids. Residues of the PCB tended to respond similarly. Residue levels in brains were greatest in little brown bats; the maximum level of the PCB, 7.9 ppm, was more than twice that of DDE.

Introduction

Several authors have postulated that organochlorine insecticides may have caused declines in bat populations (*2,7,11,12,15,16,19*). Free-living bats have been sampled for organochlorine residues in Britain (*13*), Arizona and Mexico (*17*), Australia (*1,10*), and Texas (*6*). Data also indicate that Aroclor 1260, a polychlorinated biphenyl (PCB), caused stillbirths in a Maryland colony of big brown bats (*Eptesicus fuscus*) (*4*). The extent of contamination of bat populations is only partly described by these few studies. Furthermore, proper interpretation of such residue data will not be possible until tissue levels of residues are experimentally correlated with toxicological effects.

At four ecologically diverse localities, authors sampled residues in three bat species (big brown bat; little brown bat, *Myotis lucifugus;* and eastern pipistrelle, *Pipistrellus subflavus*), which are common and wide-ranging in North America.

Materials and Methods

All three species were present at the two collection localities in the Allegheny Mountains. One locality, Round Top Mountain, has several abandoned mine tunnels adjacent to the Potomac River, 5.4 km southwest of Hancock, Washington Co., Md. Extensive apple orchards are located near this site. The second locality, Trout Cave, is adjacent to Highway 220, 5.6 km southwest of Franklin, Pendleton Co., W. Va. The surrounding area is mostly undisturbed forest. Additional information about these two sites is available elsewhere (*8,9*). Big brown and little brown bats were collected at a third locality, Montpelier Barn, at Montpelier State Historical Site, Laurel, Prince Georges Co., Md. This locality is in the urbanized corridor between Washington, D.C., and Baltimore, Md. It is surrounded by housing developments, shopping centers, and highways. Only little brown bats occur at the fourth site, the attic of the Methodist Church in North East. This is a town of 1,600 residents in Cecil Co., Md., at the northern end of the Chesapeake Bay.

Authors collected bats at or near the extremes of the animals' fat cycles in spring and fall 1973. Collection dates were: Round Top Mountain, April 3 and October 31; Trout Cave, April 12 and November 1; Montpelier Barn, April 26 and October 2; and North East Methodist Church, May 2 and October 3. Numbers of bats caught on these dates are given in Table 1. To obtain

[1] Fish and Wildlife Service, U.S. Department of Interior, Patuxent Wildlife Research Center, Laurel, Md. 20811

TABLE 1. *Summary of principal organochlorine residues in carcasses of 110 bats, Maryland and West Virginia—1973*

Sample	n	Residue levels, ppm wet weight											
		PCB		DDE		DDT		TDE		Dieldrin		Oxychlordane	
		Geom. Mean	Range	Geom. Mean	Range	Geom. Mean	Range	Geom. Mean	Range	Geom. Mean	Range	Geom. Mean	Range
Round Top Mountain													
Spring													
BBB ♂	6	1.27	0.50-2.4	11.16	4.6-67	0.86	0.41-2.1	0.22	0.11-0.50	0.55	0.34-1.1	0.20	0.15-0.31
♀	3	1.48	1.2-1.8	7.29	2.2-32	0.41	0.20-0.95	0.04	ND-0.14	0.56	0.28-0.81	0.10	ND-0.19
LBB ♂	2	7.75	6.0-10	10.78	8.3-14	1.08	0.83-1.4	0.62	0.55-0.71	0.73	0.38-1.4	0.43	0.38-0.48
EPB ♂	7	8.18	3.4-20	6.39	0.93-21	0.59	0.44-1.1	0.22	0.10-0.48	0.29	0.14-0.74	0.36	0.23-0.60
♀	3	6.01	2.3-11	3.32	2.6-4.4	0.52	0.34-0.68	0.18	0.15-0.22	0.30	0.22-0.56	0.36	0.28-0.46
Fall													
BBB ♂	3	0.77	0.55-0.91	6.35	2.9-17	0.41	0.22-1.3	ND	ND-ND	0.35	0.11-0.82	0.04	ND-0.13
LBB ♂	3	4.60	3.7-6.4	38.54	14-87	2.45	1.4-5.0	0.49	0.21-2.0	0.64	0.37-1.1	0.65	0.52-1.0
♀	1	2.3		23		2.0		0.77		1.3		0.38	
EPB ♂	5	3.76	0.60-9.1	9.72	4.0-34	0.74	0.33-1.4	0.27	ND-1.9	0.52	0.22-1.2	0.40	0.15-0.58
Trout Cave													
Spring													
BBB ♂	10	0.75	0.45-0.99	0.67	0.36-1.9	0.14	ND-0.25	ND	ND-ND	0.20	ND-0.28	0.02	ND-0.11
LBB ♂	7	4.21	1.2-26	2.83	0.69-18	0.55	0.17-3.2	0.55	ND-1.9	0.64	ND-2.2	0.45	0.07-1.9
EPB ♂	10	1.74	0.56-8.1	2.21	0.14-6.9	0.67	0.12-1.9	0.32	ND-0.96	0.14	ND-0.49	0.27	ND-0.63
♀	3	1.19	ND-2.6	2.56	1.0-12	0.83	0.12-3.2	0.49	ND-1.0	0.41	0.20-0.63	0.24	0.11-0.40
Fall													
BBB ♂	1	0.27		0.29		ND		ND		ND		ND	
♀	2	0.50	0.50-0.50	0.23	0.17-0.32	0.21	ND-0.47	ND	ND-ND	ND	ND-ND	ND	ND-ND
LBB ♂	1	10		2.9		0.96		0.14		0.18		0.29	
♀	4	4.69	1.3-12	1.90	0.85-4.9	1.60	ND-20	0.44	ND-2.2	0.22	0.13-0.31	0.35	0.18-0.61
EPB ♂	2	0.60	0.59-0.61	0.38	0.26-0.55	ND	ND-ND	ND	ND-ND	ND	ND-ND	0.19	0.10-0.28
♀	3	0.71	ND-2.9	1.38	0.35-4.2	0.15	ND-0.31	0.17	ND-0.36	0.09	ND-0.31	0.13	ND-0.21
Montpelier Barn													
Spring													
BBB ♂	4	4.99	4.1-5.7	5.32	4.5-5.9	0.70	0.63-0.86	0.23	0.18-0.35	0.50	0.43-0.62	0.81	0.66-0.93
♀	3	2.87	2.3-3.2	3.48	3.0-3.8	0.32	0.27-0.40	0.04	ND-0.11	0.51	0.44-0.58	0.40	0.31-0.58
LBB ♀	5	11.61	3.9-21	3.00	1.9-7.6	0.54	0.28-1.1	0.25	ND-0.52	1.04	0.71-1.5	1.52	1.1-2.7
Fall													
BBB ♂	2	2.50	2.4-2.6	2.05	2.0-2.1	0.42	0.39-0.45	ND	ND-ND	0.59	0.48-0.73	0.31	0.24-0.41
♀	3	0.48	0.14-1.5	0.59	0.19-2.0	0.05	ND-0.15	ND	ND-ND	0.26	0.12-0.47	0.11	ND-0.17
North East Church													
Spring													
LBB ♀	11	3.22	1.6-5.9	1.80	0.71-3.7	0.38	0.13-1.3	0.29	ND-0.87	1.01	0.45-3.2	0.52	ND-3.0
Fall													
LBB ♀	6	2.34	1.4-4.0	1.47	0.70-3.1	0.30	0.18-0.64	0.09	ND-0.18	0.70	0.24-3.2	0.63	0.31-1.2

NOTE: BBB = big brown bat.
LBB = little brown bat.
EPB = eastern pipistrelle bat.
n = number of bats sampled.

additional samples of stomach contents for chemical analysis, authors collected nine more bats in July 1973 after their evening feeding flights: on July 11 four big brown bats (3 males, 1 female) and one little brown bat (male) were collected at Montpelier Barn, and on July 25 two big brown bats (males) and two little brown bats (1 male, 1 female) were caught at Trout Cave. In sum, 119 bats were collected and analyzed.

Bats were frozen at capture and later thawed and weighed before dissection. Brains, carcasses, pooled samples of masticated insects from stomachs, and guano samples were analyzed. Wings, feet, and skin were removed and discarded, the head was severed at the base of the skull, and the brain was removed after clipping away the top of the cranium with iris scissors. Major masses of head masculature were placed with the carcass for analysis and the skull was dried and stored. The gastro-intestinal tract was removed from the remaining body portion, which was then analyzed as carcass. The occlusal tip width of the upper left canine (canine tip width, CTW) was measured using a 30X dissecting microscope and ocular micrometer. This measurement was used as an indicator of relative age (*3*). Samples were placed individually into cleaned and weighed glass jars, weighed, and refrozen until grinding.

All samples were analyzed at the Patuxent Wildlife Research Center. Personnel immunized against rabies prepared the tissue under a bacteriological hood in an isolated area of the laboratory because bat tissues can carry rabies. After extraction, no special precautions were required. The material was thawed and ground with anhydrous sodium sulfate to remove moisture. The resultant mixture was transferred to a paper extraction thimble and extracted with hexane on a Soxhlet apparatus for approximately 7 hours. The extract was cleaned

on a florisil column with 200 ml of 6 percent ethyl ether in hexane.

Pesticides and polychlorinated biphenyls (PCB's) were separated into three fractions on a Silicar column and analyzed with a Hewlett-Packard 5753 gas-liquid chromatograph equipped with a Ni^{63} detector, automatic sampler, digital integrator, and a 4 percent SE-30/6 percent QF-1 column at 190°C. The flow rate of 5 percent methane in argon was 60 ml/min for columns and 40 ml/min for purge. DDE was quantitated by peak height to avoid errors from PCB interference; other pesticides were measured by digital integration of area, and the PCB was quantified by comparing total peak area with that of Aroclor 1260, the compound whose pattern matched it most closely.

Samples were analyzed for *p,p'*-DDE, *p,p'*-TDE, *p,p'*-DDT, dieldrin, heptachlor epoxide, mirex, oxychlordane, *cis*-chlordane and/or *trans*-nonachlor, *cis*-nonachlor, hexachlorobenzene (HCB), toxaphene, and PCB's. Average percent recoveries from spiked tissues of mallard duck (*Anas platyrhynchos*) were DDE, 96; TRE, 103; DDT, 112; dieldrin, 101; heptachlor epoxide, 104; oxychlordane, 98; *cis*-chlordane, 100; *cis*-nonachlor, 98; HCB, 69; and the PCB, 101 percent. Residue data were not adjusted for recovery. The lower limit of sensitivity was 0.1 ppm for pesticides and 0.5 ppm for PCB in carcass and guano samples. The small size of brain and stomach samples limited sensitivity to 0.5 ppm.

Residues in 12 percent of the samples were confirmed with a gas chromatograph / mass spectrometer equipped with a temperature-programmed 1 percent SE-30 column. Program rate was 2°C/min; initial temperature, 135°C, rose to a maximum of 220°C. Operating conditions were: flow rate, 35 ml/min helium; oven temperature, 200°C; flash heater, 220°C; separator, 240°C; and ion source, 290°C. The ionization potential was 70 eV, and the accelerating voltage was 3.5 kV. Results are given as ppm wet weight unless lipid weight is designated. Guano was weighed dry as it came from the roost and masticated insects were weighed as they came from stomachs.

Because the residue data were positively skewed, they were log transformed for all statistical testing. Geometric means are given for residue data. Differences between means were tested for significance using Student's *t*-test adjusted for sample size (*18*). Significance levels were: *=$0.05>P>0.01$; **=$0.01>P>0.001$; and ***=$P<0.001$. Residue levels reported as not detected (ND) entered computations as zeros.

Results and Discussion

RESIDUES ACCORDING TO AGE

When the 119 bats sampled were subdivided by species, locality, and sex, four groups remained which included ten or more bats each: female little brown bats at North East Methodist Church (n=17); male big brown bats at Trout Cave (n=13); male pipistrelles at Trout Cave (n=12); and male pipistrelles at Round Top (n=12). For each of these four groups, the regression between CTW and μg of residue in the carcass was calculated for the PCB, DDE, DDT, TDE, dieldrin, and oxychlordane. DDE declined significantly with increased CTW among male pipistrelles from Trout Cave (r=0.63*, slope=-1.42). Similarly, the PCB declined among female little brown bats at North East Methodist Church, but the correlation coefficient was not significant (r=-0.46, $0.1>P>0.05$, slope =-0.81).

These negative relationships resemble those found for the PCB in female big brown bats and their newborn young from both Montpelier Barn (*4*) and a house attic in Gaithersburg, Md. (*5*). They differ, however, from the relationship of DDE in female free-tailed bats (*Tadarida brasiliensis*), which dropped abruptly after the first year of life and then increased with age (*6*). For the data at hand, the overall effect of age on residue load is minor and was ignored in subsequent analysis.

RESIDUES ACCORDING TO SEX

After subdividing samples by species, locality, and season, authors were able to conduct eight tests between means for males and females for the PCB, DDE, DDT, dieldrin, and oxychlordane, and seven tests for TDE. Six of 47 tests based on total μg in carcasses showed significant differences: males had higher residues than females in all six samples. Five of the six tests were for the spring sample of big brown bats from Montpelier Barn and included the PCB (t=3.60*), DDE (t=2.63*), DDT (t=5.04**), TDE (t=3.67*), and oxychlordane (t=3.14*). The sixth was the spring sample of big brown bats from Round Top and the chemical was TDE (t=3.17*).

When residues were treated as ppm, six of six significant tests also showed males with greater residues than females. Five of the six significant tests were again from the spring sample of big brown bats from Montpelier Barn: the PCB, t=4.47**; DDE, t=4.73**; DDT, t=6.01**; TDE, t=3.84*; and oxychlordane, t=3.83*. The sixth was the fall sample of big brown bats from Montpelier Barn; the chemical was DDT (t=4.91*).

Because high residues of PCB's and DDE have been found in bat milk (*5,6*), authors believe that lactation played a role in producing these differences in residues between males and females.

None of the eight male/female tests for dieldrin showed a significant difference, but means for females, expressed as both μg and ppm, were greater than those for males in seven cases. The probability of this happening if the sexes were equally likely to show a greater [illegible] in any single comparison is P=0.03*. Thus the

kinetics of dieldrin in males and females may be unique among these toxicants.

Even though significant differences involved only big brown bats, it seems clear that comparisons of samples with markedly different proportions of males and females must be made cautiously regardless of species.

RESIDUES ACCORDING TO SEASON

After subdividing samples by species, locality, and sex, authors were able to conduct 10 tests between means for spring and fall for the PCB, DDE, DDT, dieldrin, and oxychlordane, and 8 tests for TDE. When residues were expressed as total μg in carcasses, 10 of 58 tests showed significant differences, but 6 of these showed greater residues in the spring and 4 showed greater residues in the fall. All 10 tests involved males. Samples with significantly more residues in the spring were big brown bats at Montpelier Barn (DDE, $t=3.22$*; TDE, $t=10.15$***), big brown bats at Round Top (TDE, $t=5.12$**; oxychlordane, $t=2.79$*), big brown bats at Trout Cave (dieldrin, $t=2.36$*), pipistrelles at Trout Cave (DDE, $t=3.24$**). Samples with more residue in the fall were big brown bats at Montpelier (dieldrin, $t=3.46$*), little brown bats at Round Top (oxychlordane, $t=3.40$*), and pipistrelles at Round Top (DDT, $t=2.35$*; dieldrin, $t=2.34$*).

Both significant tests with TDE showed higher residue in the spring. The spring mean for TDE was greater than that for fall in seven of eight cases ($P=0.03$*). Corresponding decreases in DDT did not occur during hibernation; thus increased TDE through breakdown of DDT is not indicated.

In sum, no spring/fall pattern in μg residues appeared in the bats except, perhaps, for TDE.

Considering that μg residues did not change consistently with season, and that the bats store abundant fat before winter, it is predictable that residues expressed as ppm would be greater in spring. Twelve of 58 tests showed significant differences; spring amounts were greater in all 12 cases. Male samples were big brown bats at Montpelier Barn (the PCB, $t=6.42$**); DDE, $t=10.08$***; DDT, $t=4.37$*; TDE, $t=4.68$**; oxychlordane, $t=4.69$**), big brown bats at Trout Cave (the PCB, $t=3.52$**; TDE, $t=3.18$*), big brown bats at Round Top (oxychlordane, $t=3.69$**), and pipistrelles at Trout Cave (DDT, $t=2.72$*). Female samples were big brown bats at Montpelier Barn (DDT, $t=4.20$*; oxychlordane, $t=3.10$*) and little brown bats at North East Methodist Church (TDE, $t=2.31$*). Authors conclude that utilization of stored fat during winter caused residues to be more concentrated in bats in the spring.

RESIDUES ACCORDING TO LOCALITY

Data comparing quantities of residues in bats according to locality (Table 2) were restricted as much as possible and include only spring males for the big brown bat and pipistrelle. For the little brown bat, the Round Top and Trout Cave samples were also spring males, but spring females had to be used for Montpelier and North East Methodist Church. Comparisons among means for the little brown bat must be made with this difference in mind.

Authors drew several conclusions from Table 2. First, bats from Round Top consistently had the highest residues of ΣDDT, whereas bats from Trout Cave usually had the smallest amounts of all residues. Presumably the Round Top data reflect previous use of DDT in the apple orchards, and the Trout Cave data reflect the

TABLE 2. *Comparisons of quantities of residues in bats by locality, Maryland and West Virginia—1973*

	Mean residue in carcass, μg					
	PCB	DDE	DDT	TDE	Dieldrin	Oxychlordane
Big Brown Bat [1]						
Round Top	10.52[b]	87.75[a]	6.80[a]	1.72[a]	4.33[a]	1.58[b]
Montpelier	40.48[a]	43.23[a]	5.75[a]	1.89[a]	4.09[a]	6.63[a]
Trout Cave	5.82[c]	5.19[b]	1.01[b]	0.00[b]	1.46[b]	0.11[c]
Little Brown Bat [2]						
Round Top	25.83[ab]	35.67[a]	3.53[a]	2.04[a]	1.41[b]	1.40[b]
Montpelier	45.88[a]	11.85[ab]	2.18[a]	0.87[a]	4.10[ac]	6.04[a]
Trout Cave	13.44[ab]	9.02[ab]	1.79[a]	1.55[a]	1.77[bc]	1.40[b]
North East	14.02[b]	7.90[b]	1.63[a]	1.17[a]	4.46[a]	1.79[b]
Eastern Pipistrelle Bat [1]						
Round Top	23.87[a]	18.67[a]	1.72[a]	0.65[a]	0.84[a]	1.03[a]
Trout Cave	4.92[b]	6.18[a]	1.90[a]	0.85[a]	0.37[a]	0.73[a]

NOTE: Superscripts indicate statistical significance among means.
Shared superscripts indicate means that are not significantly different at a minimum of 95 percent confidence.

[1] Samples include only spring males. Sample sizes are given in Table 1.

[2] Samples are spring males from Round Top Mountain and Trout Cave; spring females are from Montpelier and North East. Sample sizes are given in Table 1.

absence of agriculture and industry from that area. Second, residues of PCB and oxychlordane were highest at Montpelier Barn for the two species that occur there. Sources of PCB's in such urban situations are diffuse and difficult to identify (*14*). Oxychlordane may come from household usage of chlordane on ornamental vegetation or it may come from efforts to control termites. Third, whereas most residues seem low at North East Methodist Church when considering only the little brown bat, residues of dieldrin were high, comparable to those at Montpelier Barn. Sources of the dieldrin are not known. Because results among the species are similar, authors believe that sex differences among samples of little brown bats had little effect on the means.

Authors repeated the comparisons of Table 2 but utilized data for all bats from each locality by disregarding differences in season and sex. Even though means were changed somewhat by this procedure, the conclusions were not.

Residues in guano correspond with those in the bat carcasses, but they occurred only infrequently in stomach contents (Table 3). This result could be anticipated because guano samples were large (16-20 g), relatively dry, and originated from perhaps 50-500 different bats

TABLE 3. *Residues in masticated insect samples from bat stomachs, and in guano, Maryland and West Virginia—1973*

	Residues, ppm wet weight					
	PCB	DDE	DDT	TDE	Dieldrin	Oxychlordane
Big Brown Bat: Stomach Contents						
Montpelier [1]	ND	ND	ND	ND	ND	ND
Trout Cave [2]	ND	ND	ND	ND	ND	ND
Little Brown Bat: Stomach Contents						
Trout Cave [2]	1.40	ND	ND	ND	ND	ND
North East [3]	ND	ND	ND	ND	0.06	ND
Little Brown Bat: Guano						
Montpelier [4]	0.96	0.32	ND	ND	0.18	0.10
North East [4]	0.51	0.28	0.10	ND	0.75	ND

NOTE: ND = not detected

[1] Two pooled samples; one was from four bats and the other was from five.

[2] One pooled sample from two bats.

[3] Two pooled samples; one was from 11 bats and the other was from 6.

[4] Single sample of 16-20 g.

TABLE 4. *Comparisons of residue concentrations among bat species from Maryland and West Virginia—1973*

	Mean residues in carcass, ppm wet weight					
	PCB	DDE	DDT	TDE	Dieldrin	Oxychlordane
Round Top Mountain [1]						
LBB	7.75[a]	10.78[a]	1.08[a]	0.62[a]	0.73[a]	0.43[a]
EPB	8.18[a]	6.39[a]	0.59[a]	0.22[b]	0.29[a]	0.36[a]
BBB	1.27[b]	11.16[a]	0.86[a]	0.22[ab]	0.55[a]	0.20[b]
Trout Cave [1]						
LBB	4.21[a]	2.83[a]	0.55[a]	0.55[a]	0.64[a]	0.45[a]
EPB	1.74[a]	2.21[a]	0.67[a]	0.32[a]	0.14[b]	0.27[a]
BBB	0.75[b]	0.67[b]	0.14[b]	0.00[b]	0.20[b]	0.02[b]
Montpelier Barn [2]						
LBB	11.61[a]	3.00[a]	0.54[a]	0.25[a]	1.04[a]	1.52[a]
BBB	2.87[b]	3.48[a]	0.32[a]	0.04[a]	0.51[b]	0.40[b]

NOTE: BBB = big brown bat.
LBB = little brown bat.
EPB = eastern pipistrelle bat.
Superscripts indicate statistical significance among means.

[1] Samples include only spring males. Sample sizes are given in Table 1.

[2] Samples include only spring females. Sample sizes are given in Table 1.

feeding at various times of the year. Samples of stomach contents were smaller (0.398, 4.401, and 8.595 g for big brown bats; 1.033, 1.261, and 1.610 g for little brown bats), contained more moisture, and represented fewer bats feeding at fewer times of the year. Analyses of guano may be useful for surveying bat colonies for harmful levels of organochlorine residues.

RESIDUES ACCORDING TO SPECIES

Residues (Table 4) must be expressed as concentrations rather than as total weight because individuals of the three species sampled differ in average weight. Within samples from each locality, data are restricted to a single sex and season. Several conclusions emerge. First, where all three species occur, little brown bats and pipistrelles frequently have significantly more residues than have big brown bats. Where little brown bats and pipistrelles differ significantly, little brown bats have more residues. Second, at Montpelier Barn none of the DDT-group compounds showed significant differences between species. When all data were compiled and comparisons among species were repeated, conclusions were similar except that means for little brown bats at Montpelier Barn were higher for all six residues and the differences were significant for all compounds except DDE.

The relatively low residue accumulation by big brown bats, whether the result of smaller dietary intake, more efficient excretion, or both, may be at least partly responsible for the occurrence of this species in highly urbanized localities.

The same data in Table 4 show relatively high residue accumulation by little brown bats. Knowledge of this propensity, if it is characteristic of other species in the genus, could be important in management of the endangered gray bat (*Myotis grisescens*) and Indiana bat (*Myotis sodalis*).

RESIDUES IN BRAINS

Residues of DDE in brains may be expected to vary in relation to the ratio of DDE to lipid in the entire animal. Indeed, when DDE in carcass fat was above certain concentrations, it became measurable in brains and increased with increasing levels in carcass lipids (Fig. 1, 2). It appears that DDE residues enter the brain sooner and increase more rapidly in the little brown bat than in the big brown bat (Fig. 1). Such comparisons of present data, however, may be misleading.

Even maximum brain levels of DDE are low (Fig. 1, 2). Brain levels of DDE ranging up to 8.2 ppm were found in Maryland big brown bats (*5*). The bat with the maximum level was young, feeding entirely on milk, and contained only 140 ppm DDE in its carcass lipids. Residue data for the young bat lead authors to suspect that a greater percentage of total DDE residue is found in the brain during the first weeks of life.

For comparison, previously reported residues in free-tailed bats (*6*) are included in Figure 2. Maximal brain levels for adult free-tails are similar to those in big and little brown bats. Higher levels were found in nursing young, especially those that had been deprived of food and had fallen to the cave floor.

The dependency of brain levels of the PCB on concentrations in carcass fat is not so clear as it is for DDE (Fig. 3). Authors do not know why the PCB should be less dependent.

Brain levels of the PCB reached 7.9 ppm among adult little brown bats; this is more than twice the maximum found among adults for DDE. Experimental data are needed before the significance of this concentration of the PCB can be judged. The highest brain level of Aroclor 1260 found previously (4.8 ppm) was in a nursing neonate big brown bat that contained only 90 ppm in its carcass fat (*5*). Again, the percentage of residue in the brain may be greater during the first weeks of life. The PCB was recovered from the brain of only one pipistrelle (0.66 ppm).

In sum, adult little brown bats accumulated the greatest brain residues of both DDE and the PCB; thus this species may be more susceptible to poisoning than are the other two.

OTHER RESIDUES

In addition to the six residues discussed thus far, there were six others found in carcasses infrequently and/or in small quantities. At Round Top, four big brown bats contained up to 0.25 ppm heptachlor epoxide, and three contained traces (<0.1 ppm) of *trans*-nonachlor. Three pipistrelles contained traces of *trans*-nonachlor, and one contained a trace of *cis*-chlordane.

At Trout Cave, one big brown bat contained a trace of heptachlor epoxide. Three little brown bats contained as much as 0.44 ppm *trans*-nonachlor, three had up to 0.61 ppm *cis*-chlordane, and one contained 4.5 ppm heptachlor epoxide. One pipistrelle had 0.12 ppm heptachlor epoxide and another contained 1.1 ppm mirex.

At Montpelier Barn, 13 big brown bats contained up to 0.52 ppm heptachlor epoxide, nine contained up to 0.88 ppm HCB, eight had up to 0.45 ppm *trans*-nonachlor, five had up to 0.27 ppm *cis*-chlordane, and five contained traces of *cis*-nonachlor. Six little brown bats had as much as 4.2 ppm *cis*-chlordane, five had up to 0.54 ppm heptachlor epoxide, four had up to 0.17 ppm HCB, three contained up to 0.42 ppm *cis*-nonachlor, and two had up to 0.85 ppm *trans*-nonachlor.

At North East Methodist Church, 13 little brown bats contained up to 4.4 ppm *cis*-chlordane (12 contained less than 0.5 ppm), six had up to 1.2 ppm *cis*-nonachlor, five had up to 0.17 ppm *trans*-nonachlor, and one had 0.18 ppm heptachlor epoxide.

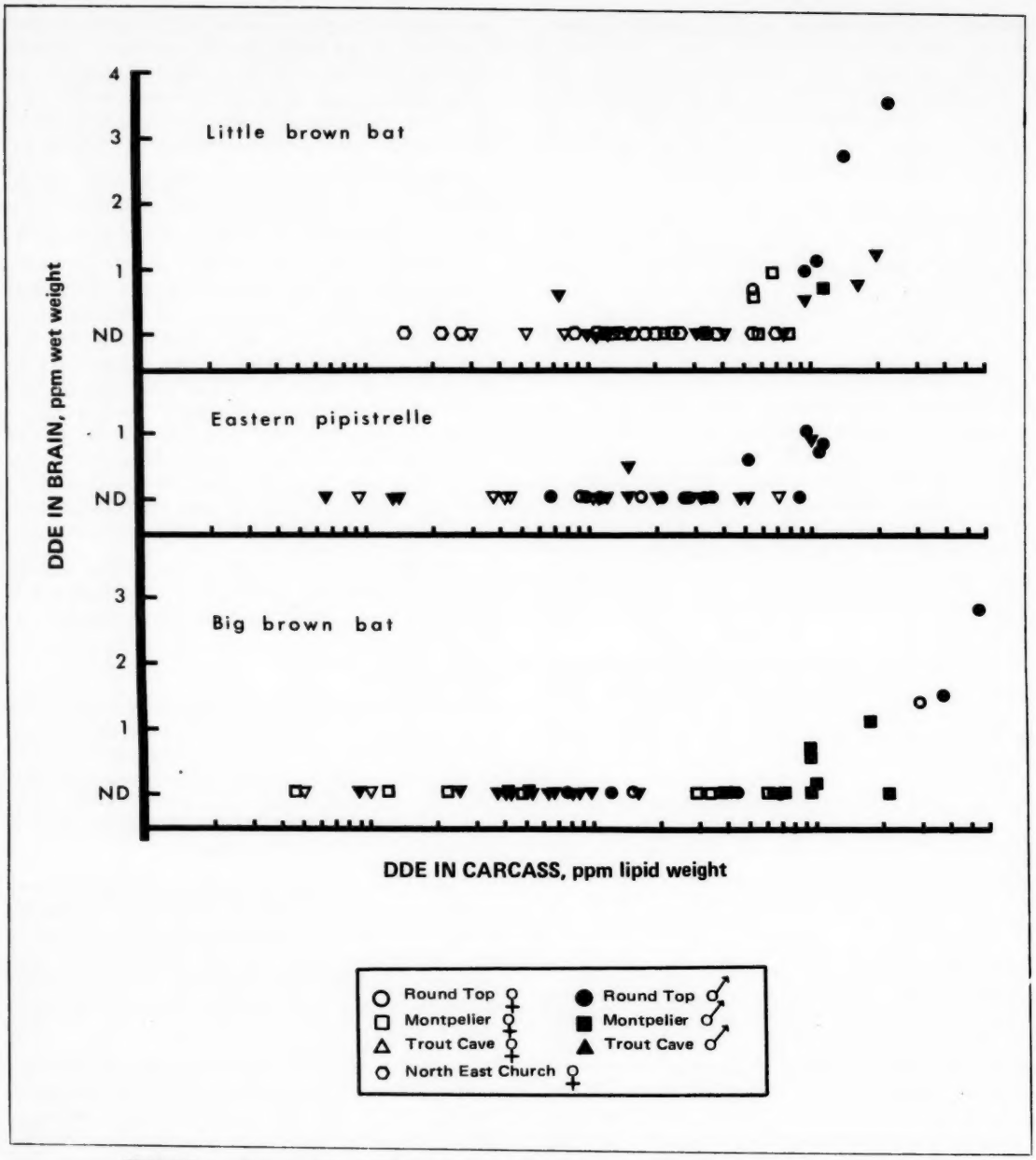

FIGURE 1. *Relationship of DDE residues in brain to those in carcass lipids of little brown bat, eastern pipistrelle, and big brown bat*

Among these lesser residues, the unique occurrence of HCB at Montpelier Barn is surprising. The source of the fungicide in this urban location is not known.

Only three bat brains that contained detectable organochlorine residues had materials other than a PCB and DDE; all three were collected in the spring. A male pipistrelle from Trout Cave had 0.46 ppm oxychlordane, and two female little brown bats from Montpelier Barn contained 0.50 ppm and 0.56 ppm oxychlordane. The latter bat also had 0.42 ppm dieldrin in its brain.

COMPARISONS WITH OTHER LOCALITIES AND SPECIES

Jefferies reported residues of DDE, DDT, and dieldrin in four pipistrelles (*Pipistrellus pipistrellus*) collected in Britain (*13*). Average carcass residues were 3.33 ppm

DDE, 1.99 ppm DDT, and 0.20 ppm dieldrin (authors' calculations). Carcass residues were given for three other bats belonging to three other species, but the highest concentrations were among the four pipistrelles. Numerous means for DDE and dieldrin from the present study (Table 1) are larger than those for the pipistrelles of Jefferies (*13*). However, for DDT, only the mean for fall-captured little brown bats at Round Top is larger than the corresponding value reported by Jefferies. The pipistrelle population sampled by Jefferies apparently experienced more direct exposure to DDT than did most populations sampled in Maryland and West Virginia. Jefferies also reported that PCB's were not found in the bats he analyzed (*13*); this differs from findings of the present study.

DDE residues in carcasses among cave populations of free-tailed bats in Arizona (*17*) and Texas (*6*) were generally lower than those in carcasses at Round Top, higher than those at both Trout Cave and North East Methodist Church, and similar to those at Montpelier Barn. PCB's were rare in free-tails, occurring in one from Arizona (1-2 ppm) and in four from Texas (0.48-1.2 ppm). Five free-tailed bats found dead on the University of Arizona campus in Tucson had apparently been exposed directly to DDT; amounts in carcasses averaged 61.4 ppm (range: 2.4-550 ppm) (*17*). Carcasses of five female big brown bats collected from a house in Tucson contained an average 117.0 ppm DDE (range: 65-160 ppm) (*17*). These values are the highest reported thus far for free-living bats.

Pooled samples from each of three bat species (*Eptesicus pumilis, Taphozous georgianus,* and *Pteropus alecto*) from the Northern Territory of Australia contained mostly trace residues (*1*). Levels reached as high as 1.82 ppm DDE, 0.25 ppm DDT, and 4.03 ppm dieldrin in the pooled whole animal samples of *E. pumilis*. PCB's were not accounted for in the analytical procedures of the Australian study (*1*). Dunsmore et al. (*10*) reported DDT and metabolites in carcasses of the Australian bat *Miniopterus schreibersii;* judging from the total μg quantities detected, average concentrations in seven samples must have ranged up to 1.4 ppm. PCB's were not reported.

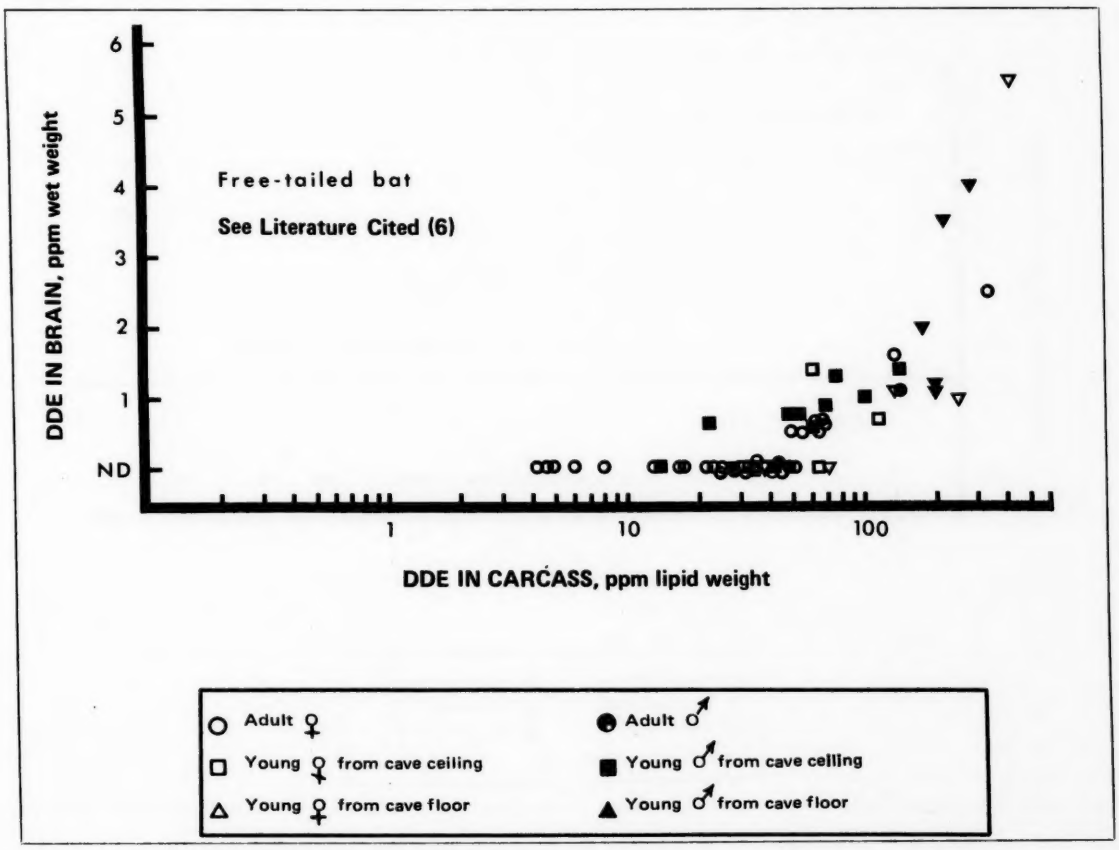

FIGURE 2. *Relationship of DDE residues in brain to those in carcass lipids of free-tailed bat*

Acknowledgments

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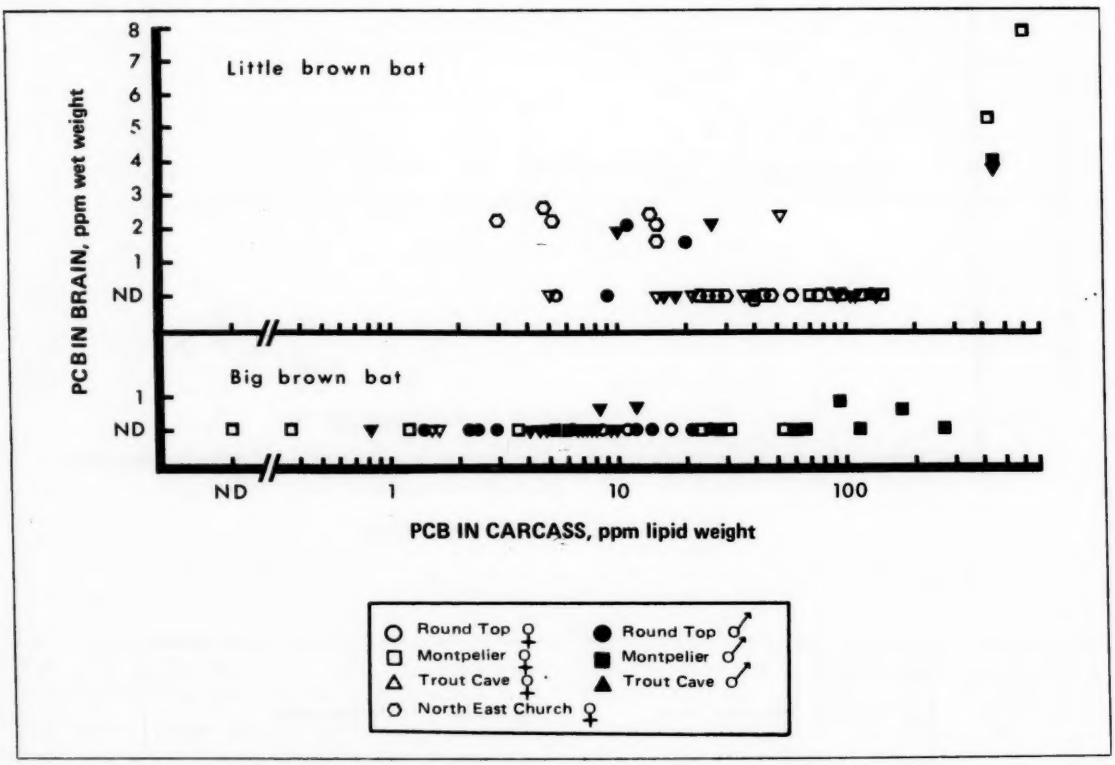

FIGURE 3. *Relationship of PCB (Aroclor 1260) residues in brain to those in carcass lipids for two bat species, Maryland and West Virginia—1973*

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RESIDUES IN SOIL

Pesticide Residues in Urban Soils from 14 United States Cities, 1970

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ABSTRACT

Soil in 14 cities was sampled and analyzed for arsenic and chlorinated hydrocarbon pesticide residues. Heavy loads of chlorinated hydrocarbon residues were detected in the soil. In addition to DDT and its metabolites, chlordane, dieldrin, endrin, heptachlor, heptachlor epoxide, and toxaphene were detected. Distinct variation appeared in some residue levels among cities. Pesticide residue levels in urban soils were generally higher than the residue levels detected in cropland soils of the same States.

Introduction

The deterioration of urban environmental quality has been the object of an increasing number of scientific investigations. Most of these have been concerned with air and water pollution. Very few investigations have focused on contamination of urban soil and fewer still on contamination with pesticides, a problem associated primarily with agricultural soils.

It has been estimated that only about half the 470 million kg active ingredients (a.i.) in pesticides and formulated products produced in the United States in 1970 were used in domestic agriculture. Most of the remaining portion is assumed to have been used by industries, public agencies, and householders (*3*). Although total pesticide use in urban and suburban areas hardly equals agricultural use, these compounds are applied to a much smaller land area. In a study of pesticide use conducted for the U.S. Environmental Protection Agency (EPA), the average amount of pesticides applied to lawns and gardens in the three cities surveyed was estimated to be between 5.9 and 11.9 kg/ha. a.i. (*3*).

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Little information has been published on pesticide residue levels in urban soil. Fahey, Butcher, and Murphy (*1*) found that 86.5 percent of the soil samples collected from Battle Creek, Mich., contained chlorinated hydrocarbon pesticide residues. In another study, Purves (*2*) found the levels of certain trace elements to be higher in urban garden plots than in rural plots.

In 1969, Wiersma, Tai, and Sand (*4*) sampled eight U. S. cities and found that the occurrence of DDT and its metabolites (DDTR) among urban sampling sites ranged from 40 percent in Houston, Tex., to 100 percent in Miami, Fla. Average DDTR residues in lawns and gardens were significantly higher than those in unkept areas within the cities. Reported here are the results for the second year of urban soil monitoring.

Sampling Procedures

Fourteen U. S. cities were selected for sampling during the summer and fall of 1970. The cities were stratified by population: there was one city with a population greater than 1,000,000; six cities between 100,000 and 1,000,000; and five cities between 25,000 and 100,000; and two cities of less than 25,000. Randomly allocated sample sites were selected within the political boundaries of each city. Sites were 231 m^2, usually 15.2-by-15.2-m plots. Sixteen soil cores, each 5.1 cm in diameter by 7.6 cm deep, were taken on an evenly spaced 4-by-4 grid. The cores were then composited, sieved through a 6.3-mm mesh, and sent for analyses to the EPA Pesticide Monitoring Laboratory in Gulfport, Miss. (now located at the NASA Mississippi Test Facility, Bay St. Louis).

Analytical Procedures

PREPARATION OF SAMPLES

A 300-g soil sample was moistened with 80 ml water and extracted with 600 ml 3:1 hexane:isopropanol by concentric rotation for 4 hours. The liquid was decanted, the alcohol was removed by three water washes,

and the hexane extract was dried through anhydrous sodium sulfate. The sample extract was then stored at low temperature for subsequent gas-chromatographic (GC) analysis.

GAS CHROMATOGRAPHY

Analyses were performed on gas chromatographs equipped with tritium foil electron affinity detectors for organochlorine compounds and thermionic or flame photometric detectors for organophosphorus compounds. A multiple-column system employing polar and nonpolar columns was used to identify and confirm pesticides. Instrument parameters were:

Columns

Glass, 6 mm OD by 4 mm ID, 183 cm long, packed with one of the following: 9 percent QF-1 on 100/120 mesh Gas-Chrom Q; 3 percent DC-200 on 100/120 mesh Gas-Chrom Q; or 1.5 percent OV-17/1.95 percent QF-1 on 100/120 mesh Sepulcoport.

Carrier Gases

5 percent methane-argon at a flow rate of 80 ml/min; prepurified nitrogen at a flow rate of 80 ml/min.

Temperatures

Detector	200°C
Injection port	250°C
Column QF-1	166°C
Column DC-200	170°-175°C
Mixed column	185°-190°C

Sensitivity (minimum detectable levels) of organochlorine compounds ranged from 0.002 to 0.03 ppm except for mixtures of polychlorinated biphenyls (PCB's), chlordane, toxaphene, etc., whose minimum detectable levels were 0.05 to 0.1 ppm. Minimum detectable levels for organophosphorus compounds were approximately 0.01 to 0.03 ppm. When necessary, residues were confirmed by thin-layer chromatography or *p*-values. The compounds detectable by this method are listed in Table 1.

Atomic absorption spectrophotometry was used to determine arsenic content. The soil sample was first extracted with 9.6N hydrochloric acid (HCl) and reduced to trivalent arsenic with stannous chloride. The trivalent arsenic was partitioned from HCl solution to benzene, then further partitioned into water for the absorption measurement. A Perkin-Elmer Model 303 instrument was used and absorbance was measured with an arsenic lamp at 1972 Å with argon as an aspirant to an air-hydrogen flame. The minimum detection limit was 0.1 ppm.

TABLE 1. *Organochlorine compounds detectable by chemical methodology of the present study*

Alachlor	Heptachlor
Aldrin	Heptachlor epoxide
Chlordane	Lindane (γ-BHC)
DDTR (*o,p'*-DDT; *p,p'*-DDT; *o,p'*-DDE; *p,p'*-DDE; *o,p'*-TDE; *p,p'*-TDE)	Methoxychlor
Dieldrin	PCB's
Endrin	PCN's
	Toxaphene
	Trifluralin

RECOVERY STUDIES

For organochlorine pesticides, the average recovery rate in soil was 90 to 110 percent. Recovery values for arsenic ranged from 70 to 80 percent. All residue levels are expressed on a dry-weight basis and are corrected for percent recovery.

Results

Results of the chemical analyses are presented in Table 2. For each city, the total number of sites is given as well as the arithmetic and geometric mean values for each residue, the range of residue values detected, and the number and percentage of sites with detectable residues.

The geometric mean estimate was used as an alternative to the arithmetic mean as a measure of central tendency for the data evaluation. Pesticide residue data frequently contain a large number of zero values, resulting either from the absence of pesticides or their presence at levels below analytical sensitivity. The data are seldom distributed normally, as shown by tests for skewness and kurtosis, but can be described by a log-normal distribution. After repeated tests for significant kurtosis and/or skewness, the ln $(X + 0.01)$ transformation was used in determining the logarithmic means. The antilogs of these figures minus 0.01 were taken to get estimates of the geometric means and 95 percent confidence intervals in the untransformed dimension (Table 2). The geometric mean estimate was calculated only for those compounds with more than one positive detection.

Of the 356 urban sites sampled, 204 or 57 percent of the sites had detectable levels of pesticide residues excluding arsenic. Residues of DDTR (the sum of all DDT isomers and metabolites) and chlordane were detected in all 14 cities. However, the frequency of occurrence within each city varied considerably. DDTR was detected in 51 percent of all samples analyzed but the frequency of detection ranged from 7 percent in Augusta, Maine, to 89 percent in Greenville, Miss. Similarly, chlordane was found in 19 percent of all samples but individual city frequencies ranged from 5 percent in Cheyenne, Wyo., to 44 percent in Grand Rapids, Mich.

Residues of heptachlor and heptachlor epoxide were detected in three and ten of the fourteen cities, respec-

TABLE 2. *Pesticide residues in soil from 14 United States cities, 1970*

Pesticide	No. Positive Sites	Percent Positive Sites	Range of Residues, ppm	Arith. Mean	Geom. Mean	95 % CI Upper	95 % CI Lower
Augusta, Maine: 27 Sites							
Arsenic	27	100.00	0.40-15.30	5.39	4.0312	5.6517	2.8746
Chlordane	3	11.1	0.21- 0.27	0.03	0.0043	0.0115	0.0000
Dieldrin	ND						
Endrin	ND						
Heptachlor	ND						
Heptachlor Epoxide	ND						
Toxaphene	ND						
o,p'-DDE	ND						
p,p'-DDE	2	7.4	0.14- 0.42	0.02	0.0027	0.0080	0.0000
o,p'-DDT	1	3.7	0.20	0.01	*	—	—
p,p'-DDT	2	7.4	0.25- 0.61	0.03	0.0031	0.0095	0.0000
o,p'-TDE	ND						
p,p'-TDE	2	7.4	0.14- 0.46	0.02	0.0027	0.0081	0.0000
DDTR	2	7.4	0.53- 1.69	0.08	0.0040	0.0128	0.0000
Charleston, S.C.: 27 Sites							
Arsenic	27	100.00	0.40-10.10	3.35	2.1325	3.1817	1.4282
Chlordane	7	25.9	1.01- 1.35	0.12	0.0094	0.0245	0.0009
Dieldrin	ND						
Endrin	ND						
Heptachlor	ND						
Heptachlor Epoxide	1	3.7	0.07	<0.01	*	—	—
Toxaphene	ND						
o,p'-DDE	1	3.7	0.03	<0.01	*	—	—
p,p'-DDE	19	70.4	0.01- 2.21	0.16	0.0417	0.0810	0.0194
o,p'-DDT	8	29.6	0.07- 8.47	0.36	0.0163	0.0417	0.0034
p,p'-DDT	17	70.0	0.06-33.80	1.54	0.0858	0.2143	0.0309
o,p'-TDE	1	3.7	0.05	<0.01	*	—	—
p,p'-TDE	15	55.6	0.03- 0.29	0.06	0.0250	0.0474	0.0113
DDTR	20	74.1	0.06-44.48	2.12	0.1589	0.3863	0.0620
Cheyenne, Wyo.: 19 Sites							
Arsenic	17	89.5	0.20- 5.50	1.23	0.5658	1.2893	0.2451
Chlordane	1	5.3	8.99	0.47	*	—	—
Dieldrin	ND						
Endrin	ND						
Heptachlor	ND						
Heptachlor Epoxide	1	5.3	0.32	0.02	*	—	—
Toxaphene	ND						
o,p'-DDE	ND						
p,p'-DDE	3	15.8	0.03- 0.09	0.01	0.0031	0.0079	0.0000
o,p'-DDT	ND						
p,p'-DDT	ND						
o,p'-TDE	ND						
p,p'-TDE	ND						
DDTR	3	15.8	0.03- 0.09	0.01	0.0031	0.0079	0.0000
Grand Rapids, Mich.: 23 Sites							
Arsenic	22	95.6	1.70-112.0	9.11	3.7194	7.2176	1.9144
Chlordane	10	43.5	0.15- 6.58	0.71	0.0556	0.1713	0.0137
Dieldrin	ND						
Endrin	ND						
Heptachlor	1	4.3	0.13	0.01	*	—	—
Heptachlor Epoxide	5	21.7	0.03- 0.23	0.02	0.0066	0.0159	0.0006
Toxaphene	ND						
o,p'-DDE	ND						
p,p'-DDE	19	82.6	0.02- 2.67	0.20	0.0564	0.1103	0.0266
o,p'-DDT	5	21.7	0.04- 0.71	0.09	0.0108	0.0295	0.0009
p,p'-DDT	19	82.6	0.05- 2.67	0.33	0.1154	0.2342	0.0544
o,p'-TDE	1	4.3	0.01	<0.01	*	—	—
p,p'-TDE	3	13.0	0.12- 0.60	0.04	0.0051	0.0144	0.0000
DDTR			0.02- 6.66	0.66	0.1833	0.3897	0.0834
Greenville, Miss.: 28 Sites							
Arsenic	27	96.4	2.60-48.90	8:10	5.4608	9.1897	3.2434
Chlordane	2	7.1	0.37- 1.40	0.06	0.0036	0.0111	0.0000
Dieldrin	1	3.6	0.48	0.02	*	—	—
Endrin	ND						
Heptachlor	ND						
Heptachlor Epoxide	ND						
Toxaphene	3	10.7	7.73-33.40	1.94	0.0119	0.0437	0.0000
o,p'-DDE	1	3.6	0.15	0.01	*	—	—
p,p'-DDE	24	85.7	0.01- 1.79	0.18	0.0641	0.1134	0.0345
o,p'-DDT	8	28.6	0.05- 0.88	0.10	0.0141	0.0335	0.0033
p,p'-DDT	25	89.3	0.02- 3.03	0.44	0.1666	0.2997	0.0907
o,p'-TDE	1	3.6	0.12	<0.01	*	—	—
p,p'-TDE	10	35.7	0.02- 0.74	0.08	0.0148	0.0330	0.0043
DDTR	25	89.3	0.05- 5.87	0.80	0.2471	0.4724	0.1270

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TABLE 2 (cont.). *Pesticide residues in soil from 14 United States cities, 1970*

Pesticide	No. Positive Sites	Percent Positive Sites	Range of Residues, ppm	Arith. Mean	Geom. Mean	95 % CI Upper	95 % CI Lower
Honolulu, Hawaii: 21 Sites							
Arsenic	21	100.00	0.50-17.40	3.34	2.1024	3.1464	1.4037
Chlordane	6	28.6	1.00-13.90	1.27	0.0406	0.1609	0.0050
Dieldrin	ND						
Endrin	ND						
Heptachlor	ND						
Heptachlor Epoxide	1	4.8	0.06	<0.01	•	—	—
Toxaphene	ND						
o,p'-DDE	1	4.8	0.12	0.01	•	—	—
p,p'-DDE	4	19.0	0.14- 0.65	0.07	0.0009	0.0257	0.0001
o,p'-DDT	1	4.8	0.11	0.01	•	—	—
p,p'-DDT	4	19.0	0.26- 0.47	0.06	0.0096	0.0274	0.0002
o,p'-TDE	1	4.8	0.33	0.02	•	—	—
p,p'-TDE	4	19.0	0.15- 0.52	0.05	0.0087	0.0242	0.0002
DDTR	4	19.0	0.57- 1.83	0.21	0.0140	0.0461	0.0003
Memphis, Tenn.: 28 Sites							
Arsenic	28	100.0	1.90-20.10	6.63	5.7837	7.1097	4.7036
Chlordane	6	21.4	0.11- 8.02	0.36	0.0138	0.0379	0.0018
Dieldrin	16	57.1	0.02-12.80	1.07	0.0525	0.1399	0.0161
Endrin	1	3.6	0.07	<0.01	•	—	—
Heptachlor	1	3.6	0.23	0.01	•	—	—
Heptachlor Epoxide	3	10.7	0.02- 0.70	0.03	0.0034	0.0095	0.0000
Toxaphene	ND						
o,p'-DDE	ND						
p,p'-DDE	12	42.9	0.01- 1.62	0.10	0.0162	0.0353	0.0052
o,p'-DDT	7	25.0	0.04- 0.24	0.03	0.0086	0.0188	0.0020
p,p'-DDT	12	42.9	0.02- 0.91	0.17	0.0319	0.0741	0.0109
o,p'-TDE	ND						
p,p'-TDE	13	46.4	0.02- 0.22	0.04	0.0159	0.0308	0.0064
DDTR	18	64.3	0.01- 2.92	0.34	0.0702	0.1582	0.0283
Mobile, Ala.: 29 Sites							
Arsenic	29	100.0	0.30- 5.20	1.12	0.8168	1.0731	0.6212
Chlordane	7	24.1	0.10- 2.50	0.18	0.0157	0.0403	0.0032
Dieldrin	3	10.3	0.04- 0.36	0.02	0.0035	0.0092	0.0000
Endrin	ND						
Heptachlor	1	3.4	0.01	<0.01	•	—	—
Heptachlor Epoxide	6	20.7	0.01- 0.09	0.01	0.0036	0.0074	0.0006
Toxaphene	ND						
o,p'-DDE	ND						
p,p'-DDE	9	31.0	0.02- 0.50	0.05	0.0109	0.0237	0.0030
o,p'-DDT	5	17.2	0.02- 0.22	0.02	0.0044	0.0100	0.0003
p,p'-DDT	9	31.0	0.02- 1.06	0.09	0.0140	0.0321	0.0037
o,p'-TDE	ND						
p,p'-TDE	9	31.0	0.02- 0.19	0.03	0.0088	0.0181	0.0027
DDTR	11	37.9	0.02- 1.37	0.19	0.0240	0.0575	0.0071
Philadelphia, Pa.: 26 Sites							
Arsenic	26	100.0	2.20-30.90	10.48	8.5081	11.1912	6.4677
Chlordane	11	42.3	0.18- 4.59	0.76	0.0705	0.2185	0.0191
Dieldrin	ND						
Endrin	ND						
Heptachlor	ND						
Heptachlor Epoxide	2	7.7	0.08- 0.11	0.01	0.0020	0.0055	0.0000
Toxaphene	ND						
o,p'-DDE	ND						
p,p'-DDE	17	65.4	0.03- 1.42	0.15	0.0431	0.0876	0.0188
o,p'-DDT	10	38.5	0.04- 1.06	0.17	0.0275	0.0681	0.0080
p,p'-DDT	19	73.1	0.04- 3.53	0.56	0.1456	0.3310	0.0610
o,p'-TDE	2	7.7	0.20- 0.45	0.03	0.0030	0.0090	0.0000
p,p'-TDE	10	38.5	0.03- 1.17	0.09	0.0181	0.0408	0.0055
DDTR	20	76.9	0.07- 6.98	1.00	0.2315	0.5492	0.0943
Portland, Oreg.: 25 Sites							
Arsenic	25	100.0	0.80-26.00	6.63	4.5113	6.5622	3.1004
Chlordane	3	12.0	0.40- 0.59	0.06	0.0059	0.0169	0.0000
Dieldrin	2	8.0	0.08- 1.19	0.05	0.0032	0.0103	0.0000
Endrin	ND						
Heptachlor	ND						
Heptachlor Epoxide	ND						
Toxaphene	ND						
o,p'-DDE	ND						
p,p'-DDE	16	64.0	0.03- 1.46	0.15	0.0413	0.0852	0.0176
o,p'-DDT	2	8.0	0.09- 0.29	0.02	0.0025	0.0075	0.0000
p,p'-DDT	11	44.0	0.07- 2.63	0.24	0.0328	0.0812	0.0101
o,p'-TDE	3	12.0	0.07-1.288	0.06	0.0045	0.0131	0.0000
p,p'-TDE	10	40.0	0.04- 3.46	0.22	0.0235	0.0582	0.0064
DDTR	17	68.0	0.03- 7.64	0.67	0.0923	0.2262	0.0343

(Continued next page)

TABLE 2 (cont.). *Pesticide residues in soil from 14 United States cities, 1970*

Pesticide	No. Positive Sites	Percent Positive Sites	Range of Residues, ppm	Arith. Mean	Geom. Mean	95 % CI Upper	95 % CI Lower
Richmond, Va.: 27 Sites							
Arsenic	26	96.3	0.10-14.80	2.39	1.2014	2.1517	0.6689
Chlordane	5	18.5	0.18- 6.42	0.51	0.0154	0.0474	0.0012
Dieldrin	4	14.8	0.07- 2.99	0.14	0.0075	0.0210	0.0000
Endrin	ND						
Heptachlor	ND						
Heptachlor Epoxide	5	18.5	0.01- 0.10	0.01	0.0034	0.0076	0.0002
Toxaphene	ND						
o,p'-DDE	2	7.4	0.09- 0.15	0.01	0.0021	0.0058	0.0000
p,p'-DDE	17	63.0	0.01- 4.24	0.35	0.0544	0.1257	0.0206
o,p'-DDT	4	14.8	0.18- 3.25	0.16	0.0081	0.0229	0.0000
p,p'-DDT	7	25.9	0.22-15.10	0.79	0.0234	0.0696	0.0040
o,p'-TDE	2	7.4	0.04- 0.46	0.02	0.0022	0.0067	0.0000
p,p'-TDE	17	63.0	0.03- 5.65	0.40	0.0509	0.1163	0.0194
DDTR	18	66.7	0.03-28.33	1.73	0.0034	0.0076	0.0002
Sikeston, Mo.: 27 Sites							
Arsenic	26	96.3	1.00- 7.20	3.00	2.2217	3.5780	1.3781
Chlordane	2	7.4	0.30- 1.19	0.06	0.0036	0.0111	0.0000
Dieldrin	1	3.7	0.33	0.01	*	—	—
Endrin	ND						
Heptachlor	ND						
Heptachlor Epoxide	ND						
Toxaphene	1	3.7	16.10	0.60	*	—	—
o,p'-DDE	ND						
p,p'-DDE	7	25.9	0.02- 0.23	0.03	0.0084	0.0187	0.0018
o,p'-DDT	2	7.4	0.12- 0.14	0.01	0.0022	0.0061	0.0000
p,p'-DDT	6	22.2	0.10- 0.49	0.06	0.0101	0.0245	0.0017
o,p'-TDE	ND						
p,p'-TDE	5	18.5	0.06- 0.21	0.02	0.0053	0.0121	0.0006
DDTR	7	25.9	0.03- 0.89	0.12	0.0147	0.0374	0.0029
Sioux City, Iowa: 22 Sites							
Arsenic	21	95.5	4.20-24.70	10.25	7.0473	13.9439	3.5593
Chlordane	4	18.2	0.30- 3.00	0.24	0.0127	0.0408	0.0001
Dieldrin	ND						
Endrin	ND						
Heptachlor	ND						
Heptachlor Epoxide	1	4.5	0.06	<0.01	*	—	—
Toxaphene	ND						
o,p'-DDE	ND						
p,p'-DDE	5	22.7	0.01- 0.43	0.03	0.0062	0.0156	0.0002
o,p'-DDT	ND						
p,p'-DDT	4	18.2	0.05- 0.19	0.02	0.0055	0.0139	0.0001
o,p'-TDE	ND						
p,p'-TDE	2	9.1	0.04- 0.07	0.01	0.0018	0.0051	0.0000
DDTR	5	22.7	0.06- 0.69	0.06	0.0094	0.0245	0.0009
Wilmington, Del.: 27 Sites							
Arsenic	24	88.9	0.60-32.00	9.10	3.5252	8.6773	1.4286
Chlordane	2	7.4	0.04- 0.07	<0.01	0.0015	0.0040	0.0000
Dieldrin	ND						
Endrin	ND						
Heptachlor	ND						
Heptachlor Epoxide	1	3.7	0.02	<0.01	*	—	—
Toxaphene	ND						
o,p'-DDE	1	3.7	0.09	<0.01	*	—	—
p,p'-DDE	11	40.7	0.01- 0.30	0.05	0.0155	0.0322	0.0055
o,p'-DDT	7	25.9	0.02- 0.26	0.03	0.0074	0.0161	0.0015
p,p'-DDT	11	40.7	0.07- 0.83	0.11	0.0246	0.0551	0.0084
o,p'-TDE	1	3.7	0.12	<0.01	*	—	—
p,p'-TDE	9	33.3	0.01- 0.60	0.06	0.0139	0.0312	0.0038
DDTR	11	40.7	0.08- 2.20	0.25	0.0362	0.0911	0.0111

NOTE: Compounds not listed were not detected in residue analyses.
ND = not detected.
Asterisk = geometric mean estimate not calculated with only one positive detection.

tively; dieldrin was detected in six and endrin in only one.

Arsenic is a naturally occurring element in soil, which accounts for its detection in 97 percent of the samples analyzed. As a result, it is difficult to determine whether the arsenic residues present reflect human-associated activity in addition to natural background levels. In the present study, geometric mean values for arsenic ranged from 0.5658 ppm in Cheyenne to 8.5081 ppm in Philadelphia, Pa.

Sampling sites in all cities except Mobile, Ala., were categorized as either lawn or waste according to the criteria established by Wiersma, et al. (*4*).

Lawn was defined thus:

1. Mowed grass close to a house, factory, or other structure.
2. Mowed grass in municipal parks or other city-owned or city-maintained land.
3. Garden or cultivated areas.
4. A yard that was in obvious proximity to a home.

Waste included:

1. Vacant lots where grass was apparently unkept.
2. Small wooded lots, brush or overgrown fields.
3. Areas such as power lines and gas lines.
4. Exposed soil around construction sites, eroded areas, and the like.

A *t*-test based on the transformed variate ln (X + 0.01) was used to compare residue levels of selected compounds in lawn and waste areas (Table 3). Residue

TABLE 3. *Statistical significance of differences between residue levels of specific chemicals in lawn and waste areas of 13 United States cities, 1970* [1]

City [2]	DDTR	Arsenic	Chlordane
Augusta, Maine	**	*	NS
Charleston, S.C.	NS	**	NS
Cheyenne, Wyo.	NS	NS	NS
Grand Rapids, Mich.	*	NS	NS
Greenville, Miss.	NS	NS	NS
Honolulu, Hawaii	*	NS	NS
Memphis, Tenn.	**	NS	NS
Philadelphia, Pa.	*	NS	*
Portland, Oreg.	**	NS	NS
Richmond, Va.	*	NS	NS
Sikeston, Mo.	NS	*	NS
Sioux City, Iowa	NS	NS	NS
Wilmington, Del.	NS	NS	NS

NOTE: NS = not significant.
* = significant ($P<0.05$).
** = highly significant ($P<0.01$).

[1] Based on *t*-tests of the transformed variate ln (× + 0.01), U.S. Environmental Protection Agency.

[2] Mobile, Ala., omitted because lawn and waste sites had not been differentiated.

levels of DDTR were significantly higher ($p<0.05$) in lawn areas than in waste areas in seven of the thirteen cities tested. Differences may reflect multiple sources of pesticide applications (e.g., householders, municipalities) within the cities. No significant difference occurred between DDTR levels in lawn and those in waste areas of southern cities; perhaps this is a subtle reflection of the extensive use of DDT in the regional agriculture before the compound was banned.

The *t*-test based on ln (X + 0.01) was also used to compare residue levels of chlordane in lawn sites with those in waste sites among all cities except Mobile. Only in Philadelphia were the chlordane levels in lawns significantly higher than in waste areas. In three of the thirteen cities arsenic levels in lawns were significantly greater ($p<0.05$) than in waste areas. Perhaps human-associated activity is responsible for this difference;

TABLE 4. *Comparison of selected compounds in urban and cropland soils of 12 States, 1970* [1,2]

	Mean Residues, ppm dry wt		
	Arsenic	DDTR	Chlordane
Maine			
Augusta	4.0312	0.0040	0.0043
	*	NS	NS
Cropland [3]	7.7028	0.0220	0.0016
South Carolina			
Charleston	2.1325	0.1589	0.0094
	NS	NS	NS
Cropland	1.3588	0.3110	0.0031
Wyoming			
Cheyenne	0.5658	0.0031	0.0043
	NS	NS	NS
Cropland [4]	0.3003	ND	0.0095
Michigan			
Grand Rapids	3.7194	0.1833	0.0556
	NS	**	**
Cropland	3.4326	0.0064	0.0018
Mississippi			
Greenville	5.4608	0.2471	0.0036
	NS	NS	NS
Cropland	5.0177	0.6326	0.0008
Tennessee			
Memphis	5.7837	0.0702	0.0138
	NS	**	NS
Cropland	6.9335	0.0102	0.0050
Alabama			
Mobile	0.8168	0.0240	0.0157
	NS	**	NS
Cropland	0.2747	0.2247	0.0016
Pennsylvania			
Philadelphia	8.5081	0.2315	0.0705
	NS	**	**
Cropland	7.1960	0.0125	0.0131
Virginia			
Richmond	1.2014	0.0034	0.0154
	NS	NS	**
Cropland [5]	1.2054	0.0038	0.0038
Missouri			
Sikeston	2.2217	0.0147	0.0036
	*	**	NS
Cropland	4.0719	0.0021	0.0063
Iowa			
Sioux City	7.0473	0.0094	0.0127
	**	*	NS
Cropland	2.4065	0.0025	0.0092
Delaware			
Wilmington	3.5252	0.0362	0.0015
	NS	NS	NS
Cropland [6]	4.2810	0.0091	0.0123

NOTE: ND = compound not detected.
NS = urban/cropland difference not significant.
* = urban/cropland difference significant ($p<0.05$).
** = urban/cropland difference highly significant ($p<0.01$).

[1] Cropland data from National Soils Monitoring Program, FY-70, unless otherwise indicated.

[2] Comparisons for Honolulu, Hawaii, and Portland, Oreg., omitted because no cropland data are available.

[3] New England States' data: Connecticut, Maine, Massachusetts, New Hampshire, Rhode Island, and Vermont.

[4] Cropland data from National Soils Monitoring Program, FY-69.

[5] Virginia/West Virginia data.

[6] Mid-Atlantic States' data: Delaware, Maryland, and New Jersey.

however, the question cannot accurately be resolved here. Natural arsenic levels in soil are dependent on parent material and most urban soil profiles are disturbed by such actions as construction, removal of topsoil, or use of fill from other areas.

Table 4 compares geometric means of three selected residues in urban soils and cropland soils in the same State or agricultural region. Generally, DDTR and chlordane residues detected in urban soils were higher than residues in corresponding cropland soils from those States or groups of States. However, there were statistically significant differences ($p<0.05$) between the geometric means of DDTR for corresponding urban and cropland soils in only six of thirteen locations and significant differences for chlordane in only three of thirteen locations.

Conclusions

The cities sampled in 1970 generally had heavy loads of chlorinated hydrocarbon pesticides in soil. This coincides with results of the previous year's urban sampling published by Wiersma et al. (*4*). In over half the thirteen cities tested in 1970, DDTR residues in lawn areas were significantly higher than in waste and unkept areas. There appeared to be some distinct variation in pesticide residue levels among cities. Finally, pesticide residue levels were generally higher in urban soils than in cropland soils of the same States.

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RESIDUES IN WATER

Distribution of Pesticides and Polychlorinated Biphenyls in Water, Sediments, and Seston of the Upper Great Lakes—1974

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ABSTRACT

Samples of water, seston, and sediment from the upper Great Lakes were collected during the summer of 1974 for analyses of polychlorinated biphenyls (PCB's), 15 organochlorine pesticides, and 17 organophosphorus pesticides. Samples were taken from 9 sites in Lake Huron, 2 in the North Channel, 5 in Georgian Bay, and 17 in Lake Superior. In the water samples all compounds analyzed were below quantification limits and traces of lindane were found in each sample. In seston samples, PCB's were above quantification limits at nearly every station and some traces of dieldrin and DDE were measured. Sediments contained PCB compounds at all stations. Dieldrin was occasionally observed, and DDT and/or its derivatives DDE and TDE were found in over one-third of all samples. No clear correlation was found between quantities of these compounds in sediments and either the percentage of clay or organic matter in the samples. Nor were any definite geographic trends present in terms of distributions observed, although concentrations were higher in areas of higher sedimentary deposition such as deeper basins. No organophosphorus compounds were detected in any sample. The highest level of DDT residues detected, 20 ppb, was lower than levels found in other studies in the lower Great Lakes and some tributary river sediments of Georgian Bay. In general, DDT residues were higher in Lake Huron and Georgian Bay sediments than in Lake Superior although PCB's were higher in some Lake Superior sediments.

Introduction

Except for limited literature on tributaries (*3,14*) no information is available in the literature regarding levels of organochlorine and organophosphorus pesticides and polychlorinated biphenyls (PCB's) in water and sediments of Lakes Superior and Huron including Georgian Bay. In order to investigate the occurrence of these compounds, a survey cruise was conducted on the upper Great Lakes in late July and early August 1974, and samples of water, sediments, and seston (suspended particulate material consisting of plankton and both inorganic and organic detrital materials) were collected. Sampling was confined to open lake waters.

This study is part of the Upper Lakes Reference Group research program on Lakes Superior and Huron, a program under the auspices of the International Joint Commission (IJC).

Sampling

Figure 1 indicates the approximate locations of sampling stations which were chosen on the basis of proximity to major rivers, industrial plants, or municipal areas. Because a fairly large vessel was employed, no station was nearer to shore than 1 km except channel stations 18 and 30. Hence samples do not reflect immediate influence from these source areas. Several background central lake sites were also chosen. The collection and analysis procedures for the three sample types are given below.

WATER

Samples were collected using a 6-liter Van Dorn bottle triggered at a depth of 1 m. Two liters of this sample were filtered through a 47-mm-diameter Whatman GF/C filter and refrigerated in acid-washed glass bottles. After approximately 30 days in storage at 4°C in the dark, samples were extracted by procedure B described in the *Analytical Methods Manual* under "Procedure for the Analysis of Organochlorinated Pesticides and PCB's in Water" (*9*). Florisil cleanup was not used because backgrounds were free of interfering substances. Filters were not analyzed. After electron-capture gas-chromatographic (GC) analysis for organochlorine pesticides and PCB's, residues of the extracts were further examined for organophosphorus pesticides by gas chromatography using flame photometric detection in both phosphorus and sulfur modes. Gas-chromatographic procedures for the organophosphates are outlined in other publications (*18,19*) but the

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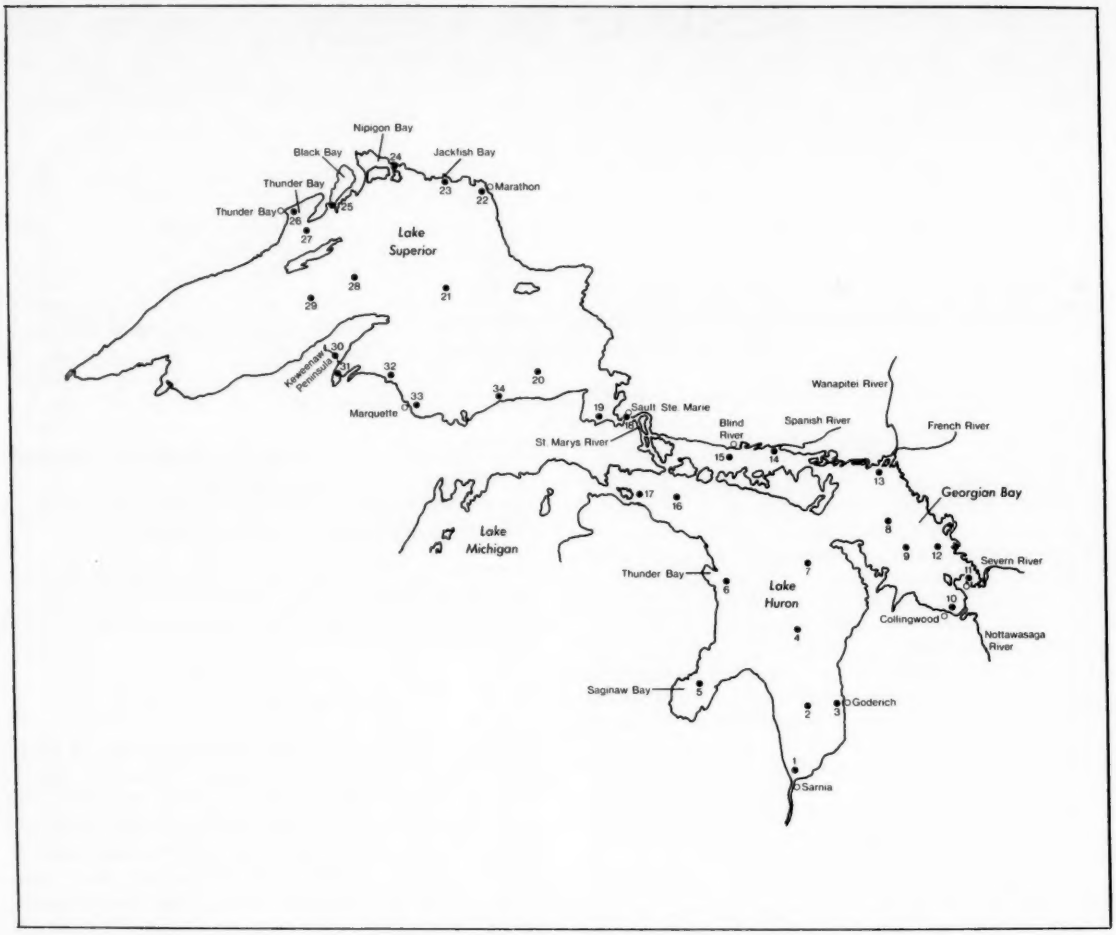

FIGURE 1. *Upper Great Lakes sampling stations*

preparation and extraction of organophosphorus samples under the same conditions as the organochlorines is an untested procedure.

SESTON

Sampling occurred whenever the vessel reached the stations and, as a consequence, seston masses and hence the concentrations therein may not be strictly comparable from station to station. Samples were collected with a plankton net which swept a cross-section of 0.126 m^2 (40 cm diameter). It was dragged 2 m from the bottom or else 100 m deep, whichever was more shallow. Collected material was passed through GF/C filters and stored, frozen and dark, in glass jars. They were subsequently homogenized in acetonitrile and the homogenate plus washings were treated according to methods outlined in the *Analytical Methods Manual* under "Procedure for the Analysis of Organochlorinated Pesticide and PCB's in Fish and Sediments" (9). The extracts were further examined for organophosphates using the GC flame photometric detector system indicated for water samples. Since very little material was available on the filters and the filters were not preweighed, the seston yield could not be determined directly. Instead, a mean of a second box of filters (72.9 $\pm$ 1.1 mg) was obtained and subtracted from the weight of the dried seston plus filters.

SEDIMENTS

Shipek surface samples were obtained at each station and stored frozen in polyethylene bags until analyzed. In previous studies at the Canadian Centre for Inland Waters, the bags have not contaminated samples except with phthalates, which do not interfere with the analyses discussed here. The Eh of the sediments was measured at the time of sampling and examination for sediment type performed later at the laboratory. Separate 10-g subsamples were employed for detecting moisture and toxic organics. Moisture content was determined by weighing the subsample before and after 48 hours dry-

ing at 135°C. Toxic organics were analyzed as recommended in the *Analytical Methods Manual* under "Procedure for the Analysis of Organochlorinated Pesticide and PCB's in Fish and Sediments" (*9*). The extraction step was carried out by ultrasonic dispersion in a 1:4 water:acetonitrile solution rather than by homogenization and, as in the water samples, organophosphorus pesticides were examined in the extract residues.

Analysis

The PCB's and 15 organochlorines have been tested for stability in tap water at 4°C in the dark (A.S.Y. Chau, Water Quality Branch, Inland Waters Directorate, 1971: unpublished results). Except for heptachlor, quantitative recoveries of 80-100 percent were obtained in all cases after 6 weeks in storage. Additional details are available in other publications (*9* and citations therein). Stability of deep-frozen seston and sediment has not been determined.

Liquid-liquid partitioning and florisil cleanups were used for the seston and sediment samples. These, coupled with quantitative identification on three or more GC columns of varying polarity, were considered adequate confirmation of compound identity. Columns employed were:

3 percent OV-101 on 80/100 mesh Chromosorb W-HP

1.5 percent OV-17/1.95 percent OV-210 on 80/100 mesh Gas-Chrom Q

4 percent OV-101/6 percent OV-210 on 80/100 mesh Gas-Chrom Q

5 percent OV-210 on 100/120 mesh Gas-Chrom Q

3 percent OV-225 on 80/100 mesh Gas-Chrom Q

All chromatograms were run isothermally at 200°C (injector 250°C) with a pulsed, linearized ^{63}Ni detector at 300°C. The carrier gas was 5 percent methane in argon at 60-75 ml/min, purged at 15 ml/min. Compounds were identified and quantified using an Autolab computing integrator with a 2 percent retention window.

PCB's were quantitated using a modified version of the method of Webb and McCall (*25*) in which all GC peaks present in Aroclor 1242, 1254, and 1260 were examined and the amount of PCB was calculated by summing the contribution of each peak. PCB's and *p,p'*-DDE could be readily resolved on column 3 and *p,p'*-DDT was further confirmed by dehydrochlorination of the concentrate using a solid matrix derivatization technique (*2*).

Analytical limits of each compound for the sample types examined are given in Tables 1 and 2. These figures are the quantification levels, the lowest level to which an analytical laboratory will attach a quantity. In general, the detection limit is a level at which the compound is observable but not quantifiable. For such, the designation TR for trace is employed and it is generally about 10 percent of the quantification limit.

TABLE 1. *Quantification limits for organochlorine pesticides and polychlorinated biphenyls*

Compound	Quantification Limit		
	Water, ppb	Seston,[1] ng	Sediment, ppm
Lindane	0.005	1	0.001
Heptachlor	0.005	1	0.001
Heptachlor epoxide	0.005	1	0.001
Aldrin	0.005	1	0.001
Dieldrin	0.005	1	0.001
Endrin	0.01	10	0.001
p,p'-DDE	0.005	1	0.001
p,p'-TDE	0.005	1	0.001
p,p'-DDT	0.005	1	0.001
o,p'-DDT	0.005	1	0.001
α-Chlordane	0.01	5	0.005
β-Chlordane	0.01	5	0.005
α-Endosulfan	0.01	10	0.01
β-Endosulfan	0.01	10	0.01
p,p'-Methoxychlor	0.01	50	0.05
PCB's	0.1	10	0.01[2]

[1] Because seston weights were variable, estimated limits are given as absolute quantities rather than as a concentration. These should be compared with the absolute amounts in Table 3.

[2] The limit of quantitation for PCB's in this survey is 1/10 that of the referenced procedure as a result of evaporating the extraction solvent to 1 ml rather than 10 ml.

TABLE 2. *Quantification limits for organophosphorus pesticides*

Compound	Quantification Limit		
	Water,[1] ppb	Seston, pg	Sediment, ppm
Phorate	0.003	50	0.01
Diazinon	0.005	100	0.02
Disulfoton	0.003	50	0.01
Ronnel	0.005	100	0.02
Methyl Parathion	0.005	100	0.02
Malathion	0.005	100	0.02
Parathion	0.005	100	0.02
Crufomate	0.025	500	0.1
Methyl Trithion	0.01	200	0.04
Ethion	0.005	100	0.02
Carbophenothion	0.01	200	0.04
Imidan	0.05	1000	0.2
Azinphosmethyl	0.05	1000	0.2
Azinphosethyl	0.05	1000	0.2
Phosphamidon	0.03	500	0.1
Dimethoate	0.005	100	0.02
Fenitrothion	0.005	100	0.02

[1] Limits are half of those noted in the referenced procedures because 2-liter samples were employed. The absolute quantity that this represents, which is indicated under seston and under sediments, is calculated for sample size. In all cases, organophosphates have not been processed by the same method used to derive the original limits.

Results and Discussion

WATER

No organochlorine pesticides or PCB's were detected in the filtered water samples at levels above the quantification limits given in Table 1. There were detectable amounts of lindane in each of the water samples ex-

amined. In addition, station 4 in the middle of Lake Huron indicated trace amounts of both heptachlor and dieldrin, and station 3 off Goderich, Ontario, showed traces of *p,p'*-DDE. A study conducted in 1964-68 on 11 sites in the Great Lakes found dieldrin to be the main pesticide detected in the region, especially in the Detroit River and St. Mary's River at Sault Ste. Marie. The other two pesticides detected were BHC in the Saginaw and Detroit Rivers and lindane which was detected at a concentration of 0.003 ppb in St. Mary's River (*12*). Levels detected in the present study were similar to those reported for the Illinois waters of Lake Michigan (*21*) where such pesticides as DDT, heptachlor epoxide, and dieldrin were all below 0.001 ppb. The inability to detect PCB's in water contrasted with studies in Lakes Erie and Ontario where PCB's in surface waters average 0.027 ppb and 0.030 ppb, respectively (Canada Centre for Inland Waters, 1972: unpublished data). However, these levels are slightly below the Centre's current quantification limits in water.

SESTON

Data for the organochlorines and PCB's in the seston are given in Table 3. Quantification of seston in the water column and hence the concentration therein were calculated from the dry weight of seston plus filter minus the mean filter weight of 72.9 ± 1.1 mg.

TABLE 3. *Residues of dieldrin,* p,p'*-DDE, and PCB's in seston, upper Great Lakes—1974*

Station No.	Compound			
	Dieldrin	*p,p'*-DDE	PCB's [1]	
			Absolute Quantity, 10^{-9} g	Concentration, ppm
1	TR	ND	180	6.0
2	TR	TR	230	8.1
3	TR	ND	240	4.9
4	TR	TR	ND	
5	TR	ND	50	1.0
6	TR	TR	180	1.5
7	TR	TR	220	1.2
8	—	TR	150	2.1
10	TR	TR	170	6.7
11	TR	ND	74	1.3
12	TR	ND	140	5.9
13	ND	TR	33	0.7
14	TR	ND	26	1.0
16	TR	TR	85	0.8
17	TR	TR	32	0.5
19	TR	ND	37	0.9
20	ND	ND	TR	
22	TR	ND	30	1.1
23	TR	TR	24	1.0
24	TR	TR	TR	
25	TR	ND	95	1.3
26	TR	ND	ND	
27	TR	ND	47	0.8
28	TR	ND	49	1.3
29	TR	ND	TR	
30	—	TR	15	0.5
31	ND	ND	TR	
32	TR	ND	ND	
33	ND	ND	ND	
34	TR	ND	TR	

NOTE: TR = trace.
ND = not detected.

[1] Concentrations are based upon the difference between filter plus seston weight and the mean filter weight of 72.9 mg (±1.1 mg). The mean seston weight so derived and used was 47.0 mg with a minimum value of 23.7 mg.

Only PCB's were observed at quantifiable levels and these occurred at nearly every station. This agrees with observations of other workers who have examined the Great Lakes for the presence of these ubiquitous compounds (*10,21*). PCB concentrations in seston ranged from nondetectable or trace levels at stations 4, 20, 24, 26, 29, and 31-34 to a maximum of 8.1 ppm in station 2 in the middle of Lake Huron. Two of the highest levels, 6.7 ppm at station 10 and 5.9 ppm at station 12, were found in Georgian Bay, indicating possible local sources of this compound. It is significant that these levels are only slightly higher than PCB concentrations in oceanic zooplankton, which is probably best called seston due to the mode of collection (*5,8,20*). Although generally Lake Superior samples have lower PCB concentrations than have those of Georgian Bay and Lake Huron, there are some stations which have levels of the same magnitude: the outlet to St. Mary's River and the mouths of Black and Thunder Bays near Marathon, Ontario.

Dieldrin and *p,p'*-DDE were also observed but only in trace amounts. The former appeared almost throughout the sampling region; the latter appeared frequently in Lake Huron and Georgian Bay but only seldom in Lake Superior.

It is significant that, even in the open lake water and especially in Lake Superior, dieldrin and PCB's are present, the latter in quantifiable amounts.

SEDIMENTS

The survey placed major emphasis on sediments, which are the ultimate sink of many organic and inorganic particulate materials in the upper Great Lakes. Results of sediment analyses are given in Table 4. PCB's occurred in higher concentrations than any other substance. The two highest values, 1.3 ppm and 90 ppb, were found in Lake Superior off Marathon, Ontario (station 22), and in the middle of the lake (station 21), respectively. Lowest values were found in Lake Huron; residues in Georgian Bay were slightly higher.

DDT and its degradation products (ΣDDT) were generally higher in Lake Huron and Georgian Bay than in Lake Superior. The highest ΣDDT value was 22 ppb at station 4 which lies in the depositional Goderich Basin of Lake Huron (*24*). Half of this was analyzed as *p,p'*-DDT and half was *p,p'*-DDE, indicating lack of total degradation. Other maximum values, 20 ppb (station 10), 12 ppb (station 12), and 11 ppb (station 11), occurred in Georgian Bay. This is significant in the wake of other studies which have shown high concentrations of ΣDDT in tributaries to Georgian Bay, mainly from past insect control in recreational areas (*3,14*). At these three stations, DDE and TDE made up most of the ΣDDT analyzed, indicating active degradation of

TABLE 4. *Distribution of organochlorines in sediment, upper Great Lakes—1974*

Station No.	Sediment Type	Redox Potential, +mv	Organic Carbon, %	Concentrations, μg/g dry weight						
				PCB's	Dieldrin	*p,p'*-DDE	*p,p'*-TDE	*p,p'*-DDT	*o,p'*-DDT	DDT
1	Sand	130	0.11	TR	TR	ND	ND	ND	ND	ND
2	Sand	480	0.50	0.01	ND[1]	0.002	ND	ND	ND	0.002
3	Sand	240	—	TR	ND	ND	ND	ND	ND	ND
4	Clayey silt	460	2.70	0.01	ND	0.01	ND	0.012	ND	0.022
5	Sand	90	0.15	TR	ND	ND	ND	ND	ND	ND
6	Sand	455	0.31	TR	ND	ND	ND	ND	ND	ND
7	Clay	440	0.31	TR	TR	ND	ND	ND	ND	ND
8	Clayey sand	500	2.1	0.01	TR	0.005	ND	0.007	ND	0.012
10	Clay	300	0.94	0.02	TR	0.004	0.009	0.006	0.001	0.020
11	Sandy silt	95	3.6	0.02	ND	0.005	0.006	ND	ND	0.011
12	Silty clay	450	0.23	0.02	ND	0.003	ND	ND	ND	0.003
13	Sand	475	0.25	TR	ND	ND	ND	ND	ND	ND
14	Sandy clay	430	0.16	TR	ND	ND	ND	ND	ND	ND
15	Sand	407	0.09	0.01	ND	ND	ND	ND	ND	ND
16	Sandy clay	470	0.51	TR	ND	0.002	ND	ND	ND	0.002
17	Sand	375	0.03	TR	ND	0.005	ND	ND	ND	0.005
18	Sand	488	0.20	0.02	ND	0.005	ND	ND	ND	0.005
19	Sand	198	0.68	TR	ND	ND	ND	ND	ND	ND
20	Clayey sand	450	1.2	TR	ND	ND	ND	0.007	ND	0.007
21	Clay	493	2.4	0.09	ND	0.002	ND	0.003	ND	0.005
22	Sandy silt	165	3.1	1.3[1]	TR	ND	ND	ND	ND	ND
23	Clayey silt	475	1.3	0.01	ND	ND	ND	ND	ND	ND
24	Silty clay	120	1.4	0.02	ND	0.006	ND	ND	ND	0.006
25	Clayey silt	147	0.77	TR	ND	ND	ND	ND	ND	ND
26	Sand	138	0.12	TR	ND	ND	ND	ND	ND	ND
27	Sand	475	0.21	0.01	ND	ND	ND	ND	ND	ND
28	Clay	490	1.2	TR	ND	ND	ND	ND	ND	ND
29	Sandy clay	470	0.22	0.01	ND	ND	ND	ND	ND	ND
30	Silty clay	100	1.7	0.02	ND	0.007	0.005	ND	ND	0.012
31	Sandy silt	490	0.17	0.02	ND	ND	ND	ND	ND	ND
32	Clayey sand	500	0.26	0.02	ND	ND	ND	ND	ND	ND
33	Sand	465	—	0.01	ND	ND	ND	ND	ND	ND
34	Sand	505	0.23	0.02	ND	ND	ND	ND	ND	ND

NOTE: TR = trace.
ND = not detected.
— = not determined.

[1] Aroclor 1260

the original compound. Another high value for ΣDDT, 12 ppb, was found in Torch Lake (station 30) in the Keweenaw waterway, which is also a recreational area.

Highest values of ΣDDT were lower often by an order of magnitude than levels of ΣDDT analyzed previously in sediments of creeks draining southern Ontario tobacco-growing areas (*3,4,7,13*) and mixed agricultural areas just south of the Canadian Shield, the Bay of Quinte watershed in Lake Ontario, and the Muskoka Lake System which drains into Georgian Bay near station 12 (*14*). One study (*14*) showed mainly DDE and TDE in such sediments, but no *o,p'*-DDT or dieldrin. Results of the present survey confirm this pattern.

Areas which revealed *p,p'*-DDT (stations 4, 8, 10, 20, 21) and *o,p'*-DDT (station 10) were located in basins of high-sediment deposition (R. L. Thomas, Canada Centre for Inland Waters, 1975: personal communication), which may explain why DDT is accumulating there. The single exception was station 10 in Georgian Bay off Collingwood, Ontario. Sediments of these sites are characterized generally by the presence of either clay, clayey silt, or clayey sand and higher organic carbon content than sediments from other stations. All also have redox potentials of at least +300 mv, indicating oxidizing environments. ΣDDT, especially TDE, generally appears to be degraded at faster rates in anaerobic environments (*11,22*). The three lowest redox potentials found were at stations 5 (+90 mv), 11 (+95 mv), and 30 (+100 mv). Station 5 in Saginaw Bay is characterized by sandy sediments in an area of active sediment transport which may explain the levels of DDT and PCB's below detection limit as there are potential inputs of these compounds in the area. However, station 11 off Penetanguishene, Ontario, and station 30 in Torch Lake, Keweenaw Peninsula, Michigan, appear to be zones of deposition in terms of sediment type; both are high in TDE and DDE, indicating degradation.

Of interest are the higher levels of DDE found in the sediments of stations 16 and 17 near the Straits of Mackinac. Station 16 lies in the depositional Mackinac Basin; station 17 is in an area of undifferentiated tills and bedrock (*24*). These higher levels may represent inputs from Lake Michigan or local insect control in the recreational or urban areas of adjacent Michigan. The former hypothesis may be supported by the fact that of all the Great Lakes, Lake Michigan appears to be highest in pesticide residues evidenced by comparative fish analyses. Lake Superior fish had the lowest concentrations: one-fourth to one-seventh the level of those in Lake Michigan fish (*15-17*). Lake Huron fish occupied the middle range of all the lakes, below Ontario fish but higher than Erie fish.

The PCB data demonstrate no clear correlation between sediment concentration and either sediment texture, organic carbon content, or redox potential. ΣDDT data, however, indicate that the highest sediment concentrations of the parent compound were found in geologic basins where accumulation of sediments also tended to be higher in clay content and organic carbon, and had higher redox potential. Dieldrin was found only in trace amounts at stations 1, 7, 8, 10, and 22; there appear to be no similarities in the nature of sediment environments at these stations and the significance of these trace amounts is uncertain.

Other organochlorine compounds were below detection limits at all stations. This may be explained by use patterns. In Ontario, the major use of organochlorines is in Lake Huron watersheds for such field crops as corn, soybeans, and small grains. Previous studies indicate that the main soil residues in these areas were aldrin, dieldrin, endrin, and ΣDDT (*1,6*). Since the late 1960's, however, use of many organochlorine compounds has diminished. Aldrin and dieldrin were banned for agricultural purposes in Ontario in 1970, and DDT was banned except for two uses in 1970. One would also have expected highest residues of DDT and dieldrin from orchards and vegetable and tobacco soils. Apparently no data have been published on the limited acreages of orchards in the Georgian Bay watershed and no studies are available to determine what inputs might come from these limited areas compared to recreational or municipal inputs from the same region. Michigan corn-belt soils analyzed for residues contained only dieldrin and DDT-related compounds; however, the sampling area could influence only the southern portion of Lake Huron (*1*).

The absence of correlation between possible sources of pesticides and sediment concentration could result from causes other than the nature and transport of sediments: atmospheric input, for example. W. M. J. Strachan (Canada Centre for Inland Waters, 1975: unpublished data) found PCB levels in atmospheric precipitation at Burlington, Ontario, to range from 0.02 to 0.05 ppb on a limited number of samples; at Parry Sound on Georgian Bay levels were less than 0.02 ppb. Also detected were nine organochlorine pesticides at levels between 0.001 and 0.026 ppb; *p,p'*-DDT and α-endosulfan occurred at the highest levels. Another study of air samples at Buffalo, N.Y., on Lake Erie detected *p,p'*-DDT and *o,p'*-DDT at levels of 11.0 and 2.9 ng/m^3, respectively (*23*). Authors presume that levels of such pesticides are lower in the atmosphere over the upper Great Lakes. Unfortunately, no data exist on the magnitude of atmospheric pesticide contributions to the Great Lakes.

Conclusions

This survey indicates low concentrations of PCB's, DDT and/or its degradation products TDE and DDE, and traces of dieldrin in sediments and seston of Lakes Superior and Huron and Georgian Bay. These compounds were below detection limits in water samples. No other organochlorine compounds were detected nor were any organophosphorus compounds found in any of the samples analyzed.

The source of these compounds is not known. In the Lake Superior watershed, agriculture is very limited; hence pesticides probably are not used in great volume. Unfortunately, use patterns of pesticides in the upper Great Lakes have not been published so inputs cannot be estimated nor are data available on use patterns of pesticides in recreational or urban areas around the upper Great Lakes. Atmospheric inputs also require further study.

Consequently, it cannot be ascertained whether the low concentrations of pesticides found in the upper lakes are due to use patterns, environmental degradation of such compounds, or both. Continuing surveillance is necessary to determine whether the organochlorine compounds detected are degrading in these lakes now that uses of some compounds such as DDT and dieldrin have been banned in the area. Such a program also would indicate whether compounds such as endosulfan and chlordane, whose usage is increasing, are accumulating in the upper Great Lakes environment.

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GENERAL

Residues of Quintozene, Its Contaminants and Metabolites in Soil, Lettuce, and Witloof-Chicory, Belgium—1969-74 [1]

W. Dejonckheere,[2] W. Steurbaut,[2] and R. H. Kips [2]

ABSTRACT

Authors studied contamination of soils used to raise lettuce in greenhouses and witloof-chicory (French endive) in forcing beds. The crops had been treated with the fungicide quintozene; residues detected included quintozene, its technical impurities and metabolites hexachlorobenzene, pentachlorobenzene, pentachloroaniline, and pentachlorothioanisole. Analyses of 72 soil samples indicated that soils remain contaminated with these chemicals one or more years after application. This is attributed to the high persistence of quintozene, its impurities and metabolites, and the almost annual application of the fungicide. Analyses of the crops show that quintozene, hexachlorobenzene, and pentachloroaniline are taken up from contaminated soils, especially by lettuce. Pentachlorothioanisole, although present in the soils, was not detected in the crops.

Introduction

The fungicide quintozene [pentachloronitrobenzene (PCNB)] is used on lettuce and witloof-chicory (French endive) to control *Rhizoctonia* bottom rot and *Botrytis* gray mold rot. This practice generally produces residues of quintozene and related compounds in the marketable product (*3,4*). When applied to lettuce in a greenhouse and to witloof-chicory in a forcing bed, the fungicide is taken up by the plants from the soil. Due to the stability of the compound a large fraction of the applied dose remains in the soil after the crop has been harvested (*1,4,6*).

Successive yearly applications of quintozene to lettuce foliage or soil and to witloof-chicory soil may increase quintozene content of the soil. Residues may then be found in crops grown on soils which have not been treated during the current growing season. This explains why certain experiments have shown no correlation between the residue content in lettuce and witloof-chicory and the dose applied during that particular growing season.

In order for authors of the present study to obtain some reliable data on the degree of contamination following yearly quintozene treatments, soil samples from lettuce greenhouses and from witloof-chicory forcing beds were analyzed.

Apart from quintozene, amounts were also determined for hexachlorobenzene (HCB), pentachlorobenzene (QCB), pentachloroaniline (PCA), and pentachlorothioanisole (PCTA); these chemicals were present as a result of the quintozene treatments (Fig. 1; *8*). For a number of soils where no quintozene was applied after sampling, residues were analyzed in the lettuce

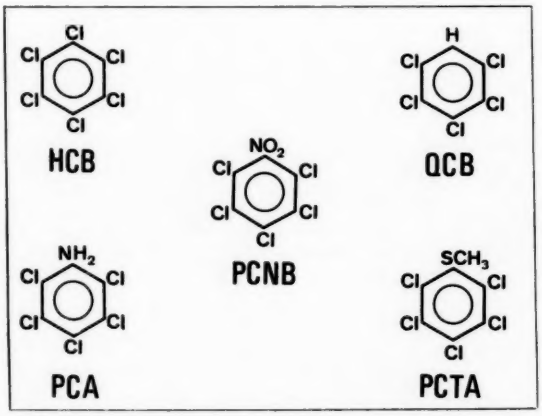

FIGURE 1. *Breakdown of PCNB: HCB and QCB are present as contaminants of the technical grade quintozene; PCA and PCTA are quintozene metabolites.*

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and witloof-chicory crops grown in these soils to determine the uptake of the compounds from the soil.

Sampling

Random soil samples were taken by inspectors of the Belgian Ministry of Agriculture. In total 72 plots were sampled: 24 from lettuce greenhouses and 48 from witloof-chicory forcing beds. Every soil composite consisted of five samples, each containing five cores of approximately 2.5 cm taken at random to a depth of 30 cm. After mixing, a subsample was taken for analysis.

The soil samples were accompanied by a statement about the quintozene treatments on the sampled area during the five previous years; information provided by the grower was sometimes vague. Samples were not air-dried nor sieved before analysis.

In order to obtain an accurate picture of the uptake of quintozene and its technical contaminants and metabolites from the soil, lettuce and witloof-chicory were sampled from plots that were not treated with quintozene during the growing season.

The 21 lettuce samples consisted of five heads taken at random in 21 greenhouses. The yellowing outer leaves were removed prior to analysis. After cutting up the leaves a subsample was taken for analysis. The 21 witloof-chicory samples which weighed about 2 kg each were taken randomly from 21 forcing beds. The crop was cleaned as customary before marketing, and cut into small pieces; a subsample was taken for analysis.

Materials and Methods

Reagents and apparatus used were:

Petroleum-ether: freshly distilled
Acetone: freshly distilled
Sodium sulfate: anhydrous, technical grade
Sodium chloride: technical grade
Ultra turax mixer: type 645 N Janke-Kunkel KG
Gas chromatographs: Varian, models 1400 and 2400, fitted with electron-capture detectors and glass columns filled with 2 percent OV-225 or 3 percent of a 3:22 OV-17:OV-210 mixture on Gas-Chrom Q.

EXTRACTION AND ANALYSIS

A 50-g soil subsample or a 100-g sample of finely chopped lettuce or witloof-chicory leaves was blended for 3 minutes with 200 ml of a 1:1 mixture of petroleum ether:acetone filtered through a Buchner filter and rinsed with 50 ml of the same solvent mixture.

The extract was transferred to a 1-liter separating funnel and shaken twice with 200 ml H_2O and 25 ml of a saturated NaCl solution. Water layers were discarded and the petroleum-ether phase was dried over anhydrous Na_2SO_4. In most cases the resulting solution was concentrated and directly analyzed by gas chromatography using the 2 percent OV-225 column. Confirmation was obtained on the OV-17—OV-210 column (Fig. 2). Recoveries ranged between 85 and 95 percent. Limits of detection for the normal procedure without concentration were: 0.01 ppm, HCB; 0.02 ppm, PCNB; 0.05 ppm, PCA and PCTA. After a tenfold concentration of the petroleum-ether extract, detection limits were one tenth the rates mentioned above (*5,6*). Dichloran and endosulfan were sometimes detected in soil samples but in much smaller amounts than quintozene and related compounds.

Results and Conclusions

Tables 1 and 2 show the results of the soil analyses and the quintozene dosage rates indicated by the growers. Tables 3 and 4 summarize the results for lettuce and witloof-chicory soils, respectively. Tables 5 and 6 show the results of soil and plant analysis for lettuce and witloof-chicory.

The recommended application rates of active ingredient (a.i.) in lettuce vary according to the references: 0.125-0.2 g/m² (*10*), 3-4 g/m² (*2*), and 8-10 g/m² (*14*). No actual dosage recommendation is available for witloof-chicory but the general tendency is to apply about 5 g a.i./m².

Information obtained from growers indicates that more quintozene is applied each year to witloof-chicory than to lettuce. This is mainly due to the facts that several crops are grown in the same year, each preceded by a quintozene treatment, and that all are grown on the same topsoil. Compounding the higher quintozene residues in witloof-chicory soils are the dark, indoor growing conditions which do not favor decomposition of the fungicide.

A certain amount of information about quintozene breakdown and metabolism has been published (*8,9, 11-13, 15*). The literature indicates that microbiological processes, influenced by temperature, humus, oxygen, and water content of the soil, influence the breakdown.

Physical processes such as evaporation and leaching may affect the rate of disappearance of pesticides from the soil. Wang and Broadbent (*15*) showed that for quintozene, evaporation plays an important part in warm and wet soils. Mainly because of the low solubility of quintozene, leaching is negligible (*13*). Dejonckheere et al. (*7*) concluded that adding organic matter to the soil increases the rate of quintozene decomposition. PCA is produced primarily under anerobic conditions; PCTA is produced under aerobic conditions.

Nevertheless the high soil residues found during the present investigation indicate that quintozene is very persistent and breaks down slowly. HCB, QCB, PCA, and PCTA were also found in easily detectable quantities associated with quintozene. As indicated in Table

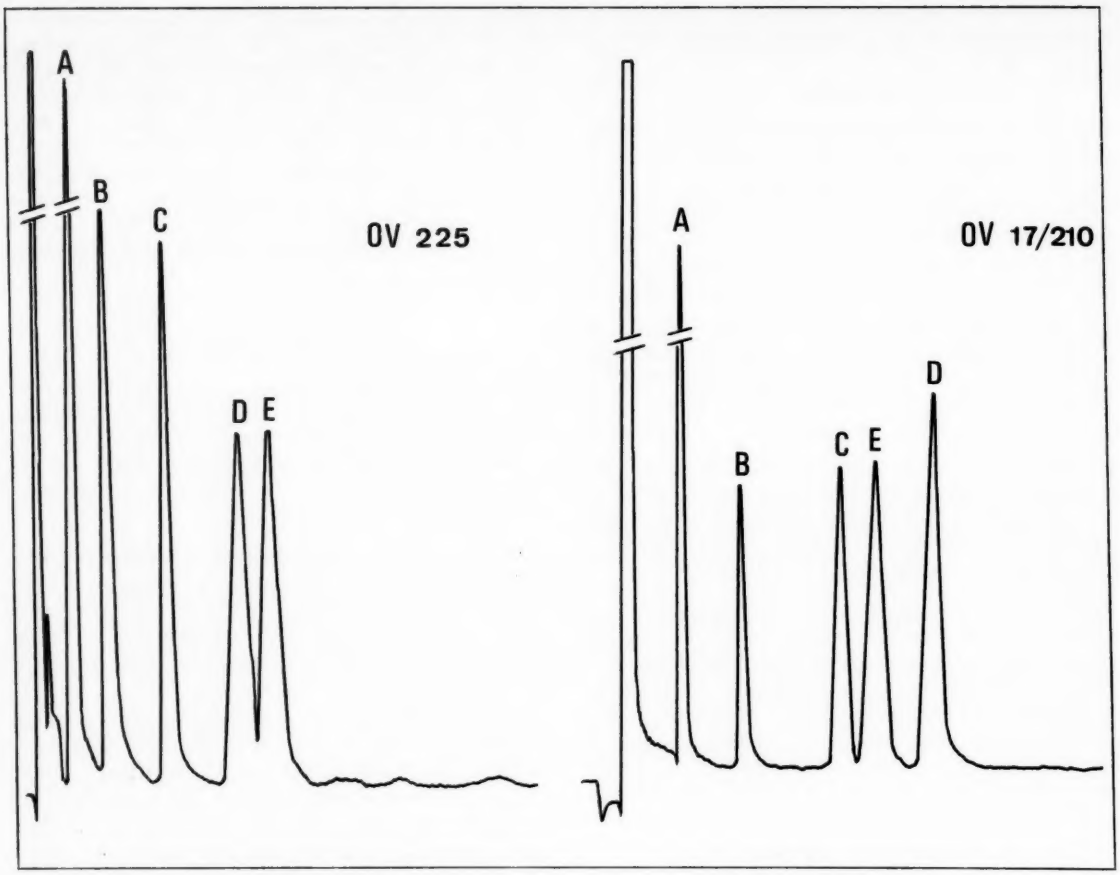

FIGURE 2. *Gas chromatograms of QCB, HCB, PCNB, PCTA, and PCA.*

TABLE 1. *PCNB, HCB, QCB, PCA, and PCTA residues in greenhouse lettuce soil, Belgium—1969–74*

	Applied Dose (a.i. g/m²)[1]							Residues, ppm				
Site	1969	1970	1971	1972	1973	1974	Total	PCNB	HCB	QCB	PCA	PCTA
1	—	1.5	0.75	0.25	1.5	0.75	4.75	4.90	0.79	0.19	1.52	0.28
2	—	—	2.92	4.0	4.0	2.00	12.92	5.80	0.31	0.19	0.98	0.74
3	—	0.46	—	0.69	—	—	1.55	1.15	0.06	0.06	0.10	0.11
4	—	—	—	0.93	—	—	0.93	1.34	0.25	0.24	0.46	0.20
5	—	0.74	0.74	0.74	0.74	—	2.96	4.40	0.38	0.30	0.88	0.55
6	—	—	—	0.93	5	2.5	8.43	0.54	0.12	0.28	0.27	0.09
7	—	4	4	1.86	1.86	0.93	12.65	3.25	1.18	0.51	3.75	1.20
8	—	4	4	4	4	2	18.00	5.10	0.98	0.40	2.06	0.37
9	—	—	3	4.5	4.5	1.5	13.5	1.83	0.23	0.41	0.78	0.11
10	4	4	4	1.6	1.6	0.8	16	5.40	1.62	0.63	1.63	0.28
11	—	2.25	2.25	4.0	4.0	—	12.5	6.40	0.41	0.28	0.94	1.08
12	2	4	4	4	4	—	18.0	6.80	0.56	0.25	0.55	0.73
13	—	4	3.6	3.2	3.6	1.56	15.96	8.40	0.98	0.27	0.84	0.92
14	—	—	—	—	0.93	—	0.93	0.97	0.08	0.06	0.14	0.15
15	—	—	—	0.93	0.93	—	1.86	1.48	0.10	0.06	0.12	0.26
16	2+2+1 (1962 and 1963)						5.0	0.08	0.11	0.03	0.53	0.11
17	—	2.8	1.86	1.30	1.30	—	7.26	0.88	0.32	0.26	0.87	0.35
18	—	—	—	0.6	0.6	0.86	2.06	1.50	0.08	0.07	0.36	0.09
19	—	—	0.4	—	0.4	—	0.8	5.50	0.42	0.42	1.05	1.48
20	1964 'til Jan. '74: 2 g/2 × per year						40	4.60	1.04	0.70	1.76	1.37
21	—	—	1.4	1.4	1.4	—	4.2	1.50	0.30	0.24	0.60	0.51
22	0.3	0.3	0.3	0.3	0.3	0.56	2.06	0.22	0.06	0.06	0.20	0.17
23	0.3	0.3	0.3	0.3	0.3	0.56	2.06	0.14	0.03	0.05	0.10	0.06
24	0.5	0.5	0.6	0.6	0.5	—	2.7	0.63	0.08	0.06	0.66	0.16
						Average		3.03	0.44	0.25	0.84	0.47

NOTE: Blank denotes no application.

[1] Dosage rates are approximations supplied by growers.

TABLE 2. *PCNB, HCB, QCB, PCA, and PCTA residues in soil of witloof-chicory forcing beds, Belgium—1969-74*

Site	Applied Dose (a.i. g/m²)[1]							Residues, ppm				
	1969	1970	1971	1972	1973	1974	Total	PCNB	HCB	QCB	PCA	PCTA
1	—	—	—	—	3	—	3	0.76	0.15	0.08	0.34	0.04
2	—	20	20	20	20	—	80	25.50	1.31	1.14	4.10	0.49
3	—	8	8	—	8	—	24	4.90	0.29	0.19	1.10	0.07
4	—	—	17.2	17.2	—	—	34.4	2.35	0.26	0.23	1.60	0.12
5	—	7	7	15	—	—	29	21.60	1.85	0.54	5.10	0.67
6	—	8	8	8	8	—	32	9.00	2.25	0.73	5.60	0.87
7	—	—	8	—	—	—	8	0.78	0.29	0.31	1.80	0.12
8	—	12	12	12	—	—	36	7.50	0.77	0.38	1.70	0.19
9	—	—	—	6	6	—	12	1.60	0.20	0.20	1.00	0.11
10	NI	NI	NI	NI	NI	NI	NI	0.67	0.20	0.14	0.68	0.03
11	NI	NI	NI	NI	NI	NI	NI	2.80	0.21	0.13	0.89	0.07
12	—	—	—	—	5	—	5	3.40	0.45	0.21	1.37	0.14
13	—	8	8	6	6	—	30	2.00	0.34	0.26	1.31	0.07
14	—	16	16	16	16	—	64	10.30	1.10	0.95	0.99	0.36
15	—	—	—	—	10	—	10	6.50	0.74	0.60	5.60	0.53
16	NI	NI	NI	NI	NI	NI	NI	23.60	4.18	1.22	13.60	1.57
17	NI	NI	NI	NI	NI	NI	NI	5.10	0.55	0.39	2.30	0.13
18	—	15	15	15	15	—	60	18.40	2.84	0.57	6.30	0.41
19	NI	NI	NI	NI	NI	NI	2	0.85	0.04	0.03	0.14	0.06
20	—	—	28	28	—	—	56	10.60	1.06	0.74	2.30	0.35
21	—	14	14	14	—	—	42	20.40	1.70	0.94	5.40	0.46
22	NI	NI	NI	NI	NI	NI	NI	6.10	0.95	1.22	0.86	0.28
23	—	5	5	5	5	—	20	2.70	0.61	0.29	2.52	0.09
24	—	5	5	5	—	—	15	3.75	0.22	0.17	1.30	0.08
25	—	4	4	4	4	—	16	3.25	0.27	0.15	0.51	0.04
26	NI	NI	NI	NI	NI	NI	NI	22.50	0.83	0.23	1.07	0.17
27	NI	NI	NI	NI	NI	NI	NI	1.85	0.25	0.21	0.83	0.07
28	—	10	10	10	10	—	40	19.50	1.40	0.72	7.90	1.02
29	—	10	10	10	10	—	40	15.80	0.81	0.43	3.50	0.25
30	—	14	14	14	—	—	42	12.10	1.28	0.70	7.10	0.58
31	—	—	7	7	—	—	14	0.25	0.08	0.04	0.14	0.06
32	—	6	6	6	6	—	24	3.95	0.52	0.38	1.58	0.15
33	—	10	10	10	10	—	40	10.90	0.62	0.20	2.18	0.16
34	—	15	15	15	15	—	60	34.30	2.30	0.48	3.00	0.41
35	—	14	14	14	14	—	56	13.40	1.20	0.67	7.10	0.78
36	—	30	30	30	30	5	125	55.60	2.06	0.56	0.80	0.41
37	—	28.5	14.25	14.25	14.25	—	71.25	10.90	0.40	0.24	1.10	0.12
38	—	—	14.25	14.25	14.25	—	42.75	2.10	0.13	0.11	0.32	0.32
39	—	—	—	—	4.30	—	4.30	0.64	0.12	0.11	0.26	0.05
40	—	—	—	14.25	4.30	—	18.55	0.74	0.40	0.25	1.40	0.10
41	—	—	—	—	8.60	—	8.60	11.80	0.81	0.80	2.20	2.61
42	NI	NI	NI	NI	NI	NI	NI	5.40	0.86	0.33	3.90	0.46
43	—	—	2.90	—	—	—	2.90	6.25	0.85	0.58	2.50	1.86
44	—	—	—	6.2	—	—	6.2	13.60	1.11	1.11	3.05	1.28
45	—	—	—	6.2	—	—	6.2	3.10	0.50	0.73	3.22	0.71
46	—	—	14	7	7	—	28	1.51	0.51	0.64	2.58	0.24
47	14	—	—	4.15	4.15	—	22.30	3.30	0.97	0.49	7.90	1.11
48	—	—	—	12	—	—	12	0.12	0.02	0.02	0.68	0.39
						Average		9.25	0.85	0.46	2.83	0.43

NOTE: Blank denotes no application.
NI denotes no information available.

[1] Dosage rates are approximations supplied by growers.

TABLE 3. *Survey of PCNB, HCB, QCB, PCA, and PCTA residues in greenhouse lettuce soil, Belgium—1969–74*

Samples containing PCNB	Range, ppm	Samples containing: HCB	QCB	PCTA	PCA	Range, ppm
3	0.0— 0.5	6	8	3	1	0.0—0.1
4	0.5— 1.0	3	2	7	5	0.1—0.2
5	1.0— 1.5	2	7	3	1	0.2—0.3
1	1.5— 2.0	6	3	2	2	0.3—0.5
—	2.0— 3.0	1	3	2	4	0.5—0.7
4	3.0— 5.0	3	1	3	6	0.7—1.0
6	5.0— 7.0	2	—	4	1	1.0—1.5
1	7.0—10.0	1	—	—	3	1.5—2.0
		—	—	—	1	2.0—3.0
		—	—	—	1	3.0—5.0
		—	—	—	—	5.0—7.0

NOTE: Blank denotes no samples in the range indicated.

TABLE 4. *Survey of PCNB, HCB, QCB, PCA, and PCTA residues in soil of witloof-chicory forcing beds, Belgium—1969-74*

Samples containing PCNB	Range, ppm	Samples containing: HCB	QCB	PCTA	PCA	Range, ppm
2	0.0— 0.5	3	3	12	—	0.0— 0.1
6	0.5— 1.0	5	8	11	1	0.1— 0.2
4	1.0— 2.0	8	10	3	2	0.2— 0.3
4	2.0— 3.0	4	8	10	2	0.3— 0.5
7	3.0— 5.0	6	8	3	3	0.5— 0.7
7	5.0—10.0	9	7	3	—	0.7— 1.0
8	10.0—15.0	7	4	3	8	1.0— 1.5
3	15.0—20.0	2	—	2	4	1.5— 2.0
5	20.0—30.0	3	—	1	7	2.0— 3.0
1	30.0—40.0	1	—	—	7	3.0— 5.0
1	50.0—60.0	—	—	—	5	5.0— 7.0
		—	—	—	4	7.0—10.0
		—	—	—	1	10.0—15.0

NOTE: Blank denotes no samples in the range indicated.

TABLE 5. *PCNB, HCB, QCB, PCA, and PCTA residues in soil and in lettuce grown in that soil, Belgium—1969-74*

	Residues, ppm									
	Soil					Lettuce				
Site	PCNB	HCB	QCB	PCA	PCTA	PCNB	HCB	QCB	PCA	PCTA
1	4.90	0.79	0.19	1.52	0.28	0.39	<0.005	ND	0.14	ND
3	1.15	0.06	0.06	0.10	0.11	0.10	0.008	ND	0.02	ND
4	1.34	0.25	0.24	0.46	0.20	0.04	<0.005	ND	0.01	ND
5	4.40	0.38	0.30	0.88	0.55	1.51	0.018	ND	0.40	ND
6	0.54	0.12	0.28	0.27	0.09	0.02	<0.005	ND	0.01	ND
7	3.25	1.18	0.51	3.75	1.20	0.63	0.038	ND	0.63	ND
9	1.83	0.23	0.41	0.78	0.11	0.22	0.010	ND	0.13	ND
10	5.40	0.98	8.40	2.06	0.37	0.83	0.037	ND	0.38	ND
11	6.40	0.41	0.28	0.94	1.08	0.61	0.009	ND	0.25	ND
12	6.80	0.56	0.25	0.55	0.73	0.60	0.010	ND	0.24	ND
13	8.40	0.98	0.27	0.84	0.92	0.57	0.010	ND	0.26	ND
14	0.97	0.08	0.06	0.14	0.15	0.75	<0.005	ND	0.31	ND
15	1.48	0.10	0.06	0.12	0.26	1.15	<0.005	ND	0.58	ND
16	0.08	0.11	0.03	0.53	0.11	0.04	ND	ND	0.01	ND
17	0.88	0.32	0.26	0.87	0.35	0.03	<0.005	ND	0.03	ND
19	5.50	0.42	0.42	1.05	1.48	0.10	0.008	ND	0.06	ND
20	4.60	1.04	0.70	1.76	1.37	0.05	0.013	ND	0.05	ND
21	1.50	0.30	0.24	0.60	0.51	0.38	ND	ND	0.21	ND
22	0.22	0.06	0.06	0.20	0.17	0.28	0.007	ND	0.09	ND
23	0.14	0.03	0.05	0.10	0.06	0.72	0.012	ND	0.18	ND
24	0.63	0.08	0.06	0.66	0.16	0.02	<0.005	ND	0.02	ND

NOTE: ND = not detectable.

TABLE 6. *PCNB, HCB, QCB, PCA, and PCTA residues in soil and in witloof-chicory forced in that soil, Belgium—1969-74*

	Residues, ppm									
	Soil					Witloof-Chicory				
Site	PCNB	HCB	QCB	PCA	PCTA	PCNB	HCB	QCB	PCA	PCTA
2	25.50	1.31	1.14	4.10	0.49	0.052	0.030	ND	0.012	ND
3	4.90	0.29	0.19	1.10	0.07	0.016	ND	ND	ND	ND
4	2.35	0.26	0.23	1.60	0.12	0.005	ND	ND	ND	ND
8	7.50	0.77	0.38	1.70	0.19	0.160	0.012	ND	ND	ND
12	3.40	0.45	0.21	1.37	0.14	0.005	ND	ND	ND	ND
14	10.30	1.10	0.95	0.99	0.36	0.023	ND	ND	ND	ND
16	23.60	4.18	1.22	13.60	1.57	0.007	0.010	ND	0.015	ND
17	5.10	0.55	0.39	2.30	0.13	0.010	0.008	ND	0.010	ND
36	55.60	2.06	0.56	3.80	0.41	0.330	0.029	ND	0.040	ND
37	10.90	0.40	0.24	1.10	0.12	0.008	0.002	ND	0.006	ND
38	2.10	0.13	0.11	0.32	0.32	0.005	ND	ND	ND	ND
39	0.64	0.12	0.11	0.26	0.05	0.005	ND	ND	ND	ND
40	0.74	0.40	0.25	1.40	0.10	0.005	0.007	ND	0.017	ND
41	11.8	0.81	0.80	2.20	2.61	0.036	0.005	ND	0.006	ND
42	5.40	0.86	0.33	3.90	0.46	0.056	0.053	ND	0.100	ND
43	6.25	0.85	0.58	2.50	1.86	0.026	0.009	ND	0.014	ND
44	13.60	1.11	1.11	3.05	1.28	0.015	0.007	ND	0.022	ND
45	3.10	0.50	0.73	3.22	0.71	0.005	ND	ND	0.007	ND
46	1.51	0.51	0.64	2.58	0.24	0.005	0.003	ND	0.005	ND
47	3.30	0.97	0.49	7.90	1.11	0.013	0.026	ND	0.130	ND
48	0.12	0.02	0.02	0.68	0.39	ND	ND	ND	ND	ND

NOTE: ND = not detectable.

1, average residues (ppm) in lettuce soil for the 6-year period were: PCNB, 3.03; HCB, 0.44; QCB, 0.25; PCA, 0.84; PCTA, 0.47. Corresponding values in witloof-chicory soil listed in Table 2 were: PCNB, 9.25; HCB, 0.85; QCB, 0.46; PCA, 2.83; PCTA, 0.43.

The average PCA:quintozene ratio was 0.290 in lettuce and 0.305 in witloof-chicory soil. The respective values for the PCTA:quintozene ratios were 0.155 and 0.046. This may indicate that more PCTA is produced during lettuce growing than during witloof-chicory growing, which corresponds to the more aerobic conditions of the lettuce field. The calculated average HCB:quintozene ratios were 0.145 for lettuce soil and 0.092 for witloof-chicory soil. QCB:quintozene ratios were 0.082 for lettuce soil and 0.048 for witloof-chicory soil. These HCB and QCB ratios seem, especially for lettuce soils, to be higher than the normal impurity content of the formulations applied, which may be explained by the rapid breakdown of quintozene and the slow formation of QCB from quintozene (*7*).

Apart from the general aspect of soil contamination which these residues present, there is also the possibility that these chemicals will be taken up by the crops grown on polluted soils. In an earlier work (*6*) the authors found that the ratio between the quintozene soil residue and the amount present in the lettuce crop at time of harvest averaged 1.34 for an early harvest (average head 143 g) and 0.44 for a late harvest (average head 315 g). For HCB these ratios were 0.97 and 0.36, respectively. The uptake was somewhat higher for low

quintozene soil residues (0.12-0.44 ppm) than for high ones (5.0-6.1 ppm). For witloof-chicory the uptake factor averaged 0.004, much lower than for lettuce.

No QCB or PCTA residues were found in the harvested crops, which confirms previous findings.

The average soil:crop quintozene ratio calculated from the results of this study was 0.15 for lettuce and 0.004 for witloof-chicory. The value for lettuce is clearly lower than that found in previous work (*6*), perhaps in part because crops in the present study were sampled for residue analysis 3-6 months after soil samples had been taken for the same purpose.

The confirmed variability in the soil:crop residue ratio for witloof-chicory may reflect the various degrees of cleanup which the plant receives before analysis. The residue level may depend greatly on the presence or absence of small quintozene-carrying soil particles between the closely packed witloof-chicory leaves.

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APPENDIX

Chemical Names of Compounds Discussed in This Issue

ALDRIN	Not less than 95% of 1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4-*endo-exo*-5,8-dimethanonaphthalene
AROCLOR 1260	PCB, approximately 60% chlorine
AZINPHOSETHYL (Guthion)	O,O-Diethyl S[4-oxo-1,2,3-benzotriazin-3(4H)ylmethyl] phosphorodithioate
AZINPHOSMETHYL	O,O-Dimethyl S[4-oxo-1,2,3-benzotriazin-3(4H)ylmethyl] phosphorodithioate
BHC (Benzene Hexachloride)	1,2,3,4,5,6-Hexachlorocyclohexane (mixture of isomers). Commercial product contains several isomers of which *gamma* is most active as an insecticide.
CARBOPHENOTHION	S-[[(*p*-Chlorophenyl)thio] methyl] O,O-diethyl phosphorodithioate
CHLORDANE	1,2,3,5,6,7,8,8-Octachloro-2,3,3a,4,7,7a-hexahydro-4,7-methanoindene. The technical product is a mixture of several compounds including heptachlor, chlordene, and two isomeric forms of chlordane.
DDD	See TDE.
DDE	Dichlorodiphenyl dichloro-ethylene (degradation product of DDT) *p,p'*-DDE: 1,1-Dichloro-2,2-bis(*p*-chlorophenyl) ethylene *o,p'*-DDE: 1,1-Dichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl)ethylene
DDT	Main component (*p,p'*-DDT): α-Bis(*p*-chlorophenyl) β,β,β-trichloroethane. Other isomers are possible and some are present in the commercial product. *o,p'*-DDT: [1,1,1-Trichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl) ethane]
DIAZINON	O,O-Diethyl O-(2-isopropyl 4-methyl-6-pyrimidyl) phosphorothioate
DIELDRIN	Not less than 85% of 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-*endo-exo*-5, 8-dimethano-naphthalene
DIMETHOATE	O,O-Dimethyl S-(N-methylcarbamoylmethyl) phosphorodithioate
DISULFOTON	O,O-Diethyl S-2(ethylthio) ethyl phosphorodithioate
ENDOSULFAN	6,7,8,9,10,10-Hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin 3-oxide
ENDRIN	1,2,3,4,10,10-Hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-*endo-endo*-5,8-dimethanonaphthalene
ETHION	0,0,0′,0′-Tetraethyl S,S′-methylene bisphosphorodithioate
FENITROTHION	O,O-Dimethyl O-(4-nitro-*m*-tolyl) phosphorothioate
HEPTACHLOR	1,4,5,6,7,8,8-Heptachloro-3a,4,7,7a-tetrahydro-4,7-*endo*-methanoindene
HEPTACHLOR EPOXIDE	1,4,5,6,7,8,8-Heptachloro 2,3-epoxy-3a,4,7,7a-tetrahydro-4,7-methanoindane
IMIDAN	O,O-Dimethyl S-phthal-imidomethyl phosphorodithioate
LINDANE	Gamma isomer of benzene hexachloride (1,2,3,4,5,6-hexachlorocyclohexane) of 99+% purity
MALATHION	S-[1,2-Bis(ethoxycarbonyl)ethyl] 0,0-dimethyl phosphorodithioate
METHOXYCHLOR	1,1,1-Trichloro-2,2-bis(*p*-methoxyphenyl) ethane
METHYL PARATHION	O,O-Dimethyl O-*p*-nitrophenyl phosphorothioate
METHYL TRITHION	O,O-Dimethyl S-(*p*-chlorophenylthio) methyl phosphorodithioate
MIREX	Dodecachlorooctahydro-1,3,4-metheno-1H-cyclobuta[cd]pentalene
NONACHLOR	1,2,3,4,5,6,7,8-Nonachlor-3a,4,7,7a-tetrahydro-4,7-methanoindan
OXYCHLORDANE	2,3,4,5,6,6a,7,7-Octachloro-1a,1b,5,5a,6,6a-hexahydro-2,5-methano-2H-indeno(1,2-β)oxirene
PARATHION	O,O-Diethyl-O-p-nitrophenyl phosphorothioate
PCB's (POLYCHLORINATED BIPHENYLS)	Mixtures of chlorinated biphenyl compounds having various percentages of chlorine
PHORATE	O,O-Diethyl S-(ethylthio) methyl phosphorodithioate
PHOSPHAMIDON	1-Chloro-diethylcarbamoyl-1-propen-2yl dimethyl phosphate
RONNEL	Dimethyl 2,4,5-trichlorophenyl phosphorothionate
TDE	2,2-Bis (p-chlorophenyl)-1,1-dichloroethane (including isomers and dehydrochlorination products)
TOXAPHENE	Chlorinated camphene (67-69% chlorine); product is a mixture of polychlor bicyclic terpens with chlorinated camphenes predominating.
TRIFLURALIN	α,α,α-Trifluoro-2,6-dinitro-N,N-dipropyl-*p*-toluidine

ERRATUM

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Information for Contributors

The *Pesticides Monitoring Journal* welcomes from all sources qualified data and interpretative information on pesticide monitoring. The publication is distributed principally to scientists, technicians, and administrators associated with pesticide monitoring, research, and other programs concerned with pesticides in the environment. Other subscribers work in agriculture, chemical manufacturing, food processing, medicine, public health, and conservation.

Articles are grouped under seven headings. Five follow the basic environmental components of the National Pesticide Monitoring Program: Pesticide Residues in People; Pesticide Residues in Water; Pesticide Residues in Soil; Pesticide Residues in Food and Feed; and Pesticide Residues in Fish, Wildlife, and Estuaries. The sixth is a general heading; the seventh encompasses briefs.

Monitoring is defined here as the repeated sampling and analysis of environmental components to obtain reliable estimates of levels of pesticide residues and related compounds in these components and the changes in these levels with time. It can include the recording of residues at a given time and place, or the comparison of residues in different geographic areas. The Journal will publish results of such investigations and data on levels of pesticide residues in all portions of the environment in sufficient detail to permit interpretations and conclusions by author and reader alike. Such investigations should be specifically designed and planned for monitoring purposes. The Journal does not generally publish original research investigations on subjects such as pesticide analytical methods, pesticide metabolism, or field trials (studies in which pesticides are experimentally applied to a plot or field and pesticide residue depletion rates and movement within the treated plot or field are observed).

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